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Coal Fired Power Plant Trace Element Study. Volume II. Station I. Volume III. Station II. Volume IV. Station III

Radian Corp, Austin, Tex

Prepared for

Environmental Protection Agency, Colo Region VIII

Sep 75

SEPTEMBER 1975

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COAL FIRED POWER PLANT TRACE ELEMENT STUDY

STATION I
STATION II
STATION III

ENVIRONMENTAL PROTECTION AGENCY
ROCKY MOUNTAIN-PRAIRIE REGION
REGION VIII

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16. ABSTRACT

This report summarizes the results of a program to characterize the trace element emissions from three coal-fired electric generating stations. A material balance approach was used for a quantitative examination of twenty-seven elements. An additional twenty-six elements were surveyed semiquantitatively. The trace elements can be broadly classed into three general groups; (1) those uniformly distributed in the coal ash, (2) those preferentially emitted with the fly ash, and (3) those emitted as vapors in the flue gas. The selection of stations using different coals with different boiler and particulate collection configurations provided a comparison of trace element emissions as a function of plant design and operating parameters. The overall report is presented in four sections. Volume I compares the three stations. Volume II includes Volume II (Station I), Volume III (Station II), and Volume IV (Station III), giving detailed results and descriptions of the methodology used for the individual stations.

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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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COAL FIRED POWER PLANT TRACE ELEMENT STUDY

VOLUME II

STATION I

SEPTEMBER 1975

PREPARED FOR

ENVIRONMENTAL PROTECTION AGENCY
REGION VIII
DENVER, COLORADO

BY

RADIAN CORPORATION
AUSTIN, TEXAS

TS-1b

FOREWORD

The four volumes comprising this document describe a coal-fired power plant trace element study prepared under EPA Contract 68-01-2663.

This work was conducted under the direction of Mr. Terry L. Thoem, Project Officer, Environmental Protection Agency, Region VIII, Denver, Colorado. The Radian program staff included Dr. F. G. Mesich as Program Manager and Dr. K. Schwitzgebel as Technical Project Director. Principle contributors were Mr. R. A. Magee, Dr. F. B. Meserole and Mr. R. G. Oldham.

Acknowledgement is given to the station personnel from each utility company whose full cooperation greatly facilitated the field work. Mr. R. M. Mann, Mrs. G. E. Wilkin and Mrs. C. M. Thompson contributed significantly to the program during sampling and analysis.

VOLUME II

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APPENDIX A - SAMPLING AT STATION I

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TABLE OF CONVERSION UNITS

To Convert From	To	Multiply By
BTU	Calories, kg	0.25198
BTU/pound	Calories, kg/kilogram	0.55552
Cubic feet	Cubic meters	0.028317
Cubic yards	Cubic meters	0.76455
Feet	Meters	0.30480
Feet/second	Meters/second	0.30480
Gallons (U.S. liq.)	Cubic meters	0.0037854
Gallons (U.S. liq.)	Liters	3.7854
Gallons/minute	Cubic meters/minute	0.0037854
Grains/cubic foot	Grams/cubic meter	2.2884
Inches	Centimeters	2.5400
Inches of H_2O (4°C)	Millimeters Hg (0°C)	1.8683
Pounds	Kilograms	0.45359
Pounds/BTU	Kilogram/Calorie, kg	1.8001
Pounds/hour	Kilograms/hour	0.45359
Pounds/standard cubic foot (60°F, 29.92 inches Hg)	Kilograms/standard cubic meter (0°C, 760 mm Hg)	15.155
Tons	Metric tons	0.90719
Yards	Meters	0.9144

STATION I SUMMARY

Station I is an example of a sub-bituminous coal-fired boiler using venturi wet scrubbers for particulate control. The sampling and characterization of trace elements in Station I streams resulted in closure of material balances for some 24 of the 27 elements examined in detail. Additional information of a semi-quantitative nature was obtained for a total of 53 elements using spark source mass spectrometry.

The distribution of the trace elements among the station exit streams as a function of coal composition and station operating configuration is essential information for the eventual development of predictive techniques. For Station I the following elements were found to be concentrated in the flue gas stream and depleted in the bottom ash stream.

Sulfur
Mercury
Chlorine
Antimony
Fluorine
Selenium
Lead
Molybdenum
Nickel
Boron
Zinc
Cadmium
Chromium
Copper
Cobalt
Arsenic
Silver
Vanadium

The following elements are distributed in proportion to the total ash flows with no concentration or depletion evident.

Barium
Beryllium
Aluminum
Calcium
Iron
Magnesium
Manganese
Titanium

The results for uranium were somewhat anomalous as it was concentrated in the bottom ash and depleted in the precipitator ash.

A detailed comparison of this station with generating stations using hot-side electrostatic precipitators and mechanical particulate collection is given in Volume I of this series.

1.0 INTRODUCTION

The use of the extensive coal resources in the Northern Great Plains area of the United States may provide a significant part of the country's energy growth for the foreseeable future. As natural gas and oil resources become less available and more costly, coal will receive increasing emphasis as a primary energy source. A coal-fired generating station produces a variety of emissions and effluents ranging from sulfur and nitrogen oxides and particulates in the flue gas to solid and liquid wastes.

In addition to carbonaceous material, coal contains inorganic matter which becomes part of the emissions and effluents from the generating station. The overall objective of this program was to define the sources, levels, and disposition of potentially toxic trace and minor elements in power plant streams. The levels of trace elements in various streams may be expected to be a function of both coal composition and plant operating configuration.

This volume describes the detailed characterization with respect to trace and minor elements of a tangentially-fired, balanced draft boiler fired with Wyoming sub-bituminous coal and using venturi wet scrubbers for particulate collection. This unit is one of four located at the power plant designated as Station I. The station has a total generating capacity of 750 MW of which the unit tested contributes 330 MW.

The following trace and minor elements were examined in detail:

Aluminum
Antimony
Arsenic
Barium
Beryllium
Boron
Cadmium
Calcium
Chlorine
Chromium
Cobalt
Copper
Fluorine
Iron
Lead
Manganese
Magnesium
Mercury
Molybdenum
Nickel
Selenium
Silver
Sulfur
Titanium
Uranium
Vanadium
Zinc

A material balance was calculated for each element to provide a sound basis for evaluating the reliability of the emissions measurements. In addition, each sample was surveyed using spark source mass spectrometry to provide a semi-quantitative assessment of additional trace elements.

The following sections give a description of the plant, a discussion of the sampling, analytical strategies, and presentation and discussion of the experimental data. Appendices are provided which describe the sampling of the plant and the analytical methodology.

2.0 SAMPLING AND SAMPLE HANDLING

The procedures used to sample Station I are described briefly in this section. Details are given in Appendix A "Sampling at Station I". Sampling was performed during the period 2-5 September 1974.

2.1 Plant Description

Unit No. 4 at Station I is a 330 MW, tangentially-fired, balanced draft boiler with three venturi scrubbers for particulate collection. The boiler is fired with Wyoming sub-bituminous coal mined near the station, transported by rail, crushed and fed to storage silos. Bottom ash is sluiced to a nearby settling pond. The scrubber slurry discharge is pumped to the same settling pond, which is the first in a series of three ponds. Ash sluice water and scrubber make-up are recycled to the plant from the last pond. The station is a base load unit. Boiler load ranged from 285-298 MW during the entire sampling period.

2.2 Sampling Points and Flow Rate Determination

The streams sampled are shown schematically in Figure 2-1. The incoming streams are coal, bottom ash sluice water, cooling tower blowdown, scrubber make-up water, and lime. Outgoing streams are bottom ash, bottom ash sluice water, economizer ash, scrubber solids, scrubber liquid, and flue gas containing fly ash. The physical location of the points for sampling these streams at the station are schematically shown in Figure 2-2.

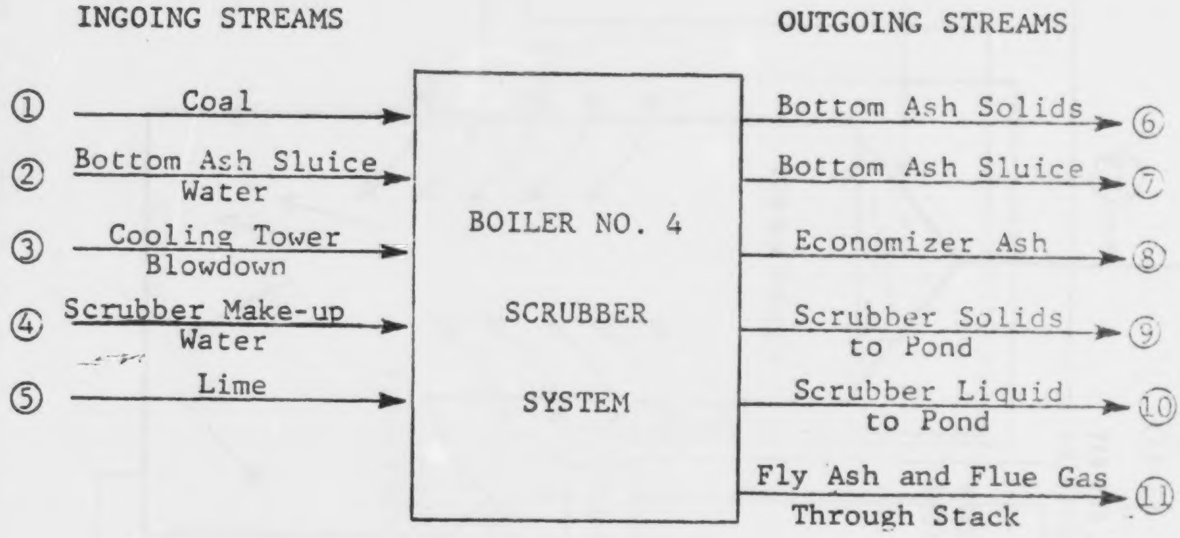
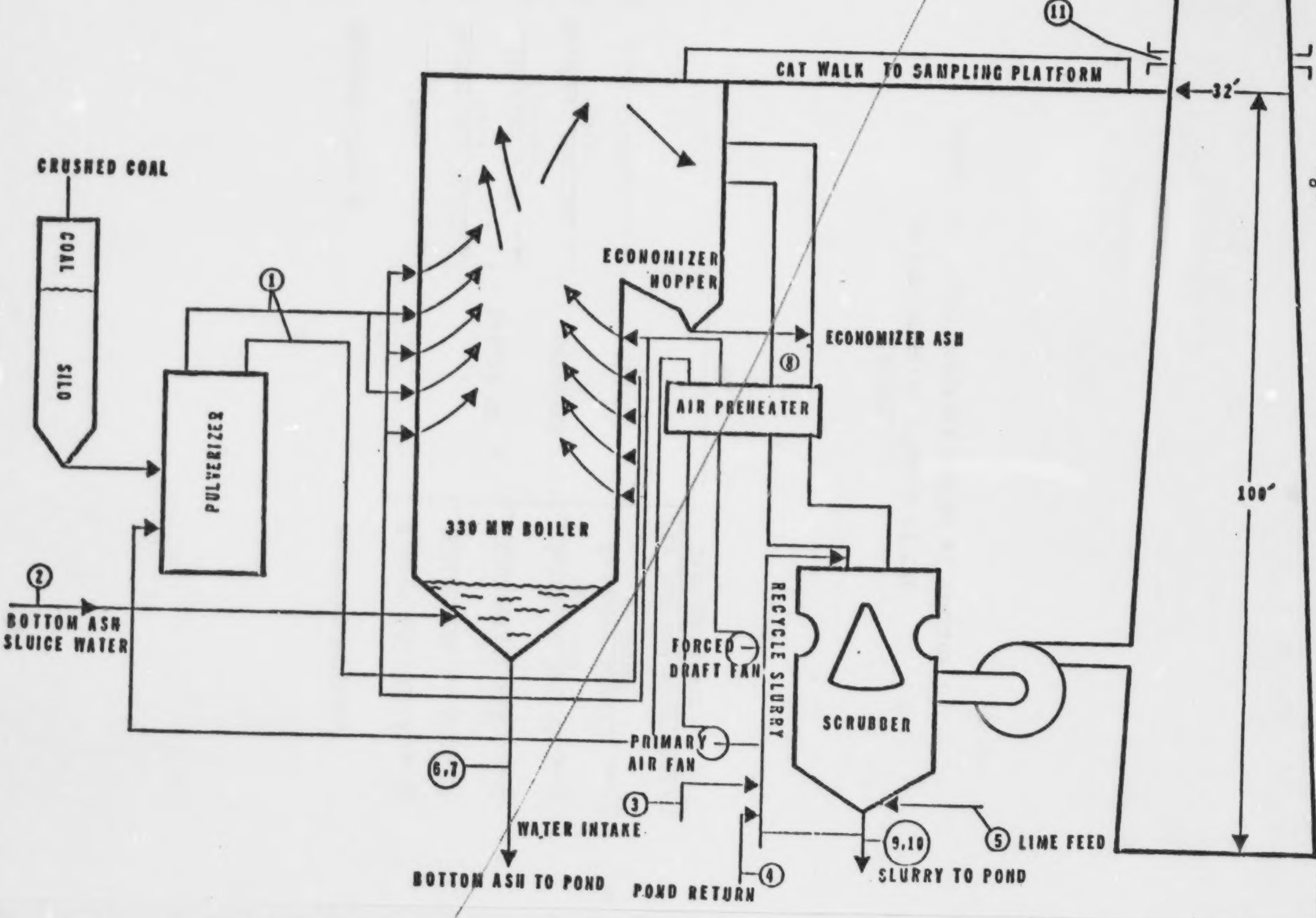

INGOING STREAMS
OUTGOING STREAMS
① Coal
② Bottom Ash Sluice Water
③ Cooling Tower Blowdown
④ Scrubber Make-up Water
⑤ Lime
BOILER NO. 4
SCRUBBER
SYSTEM
Bottom Ash Solids ⑥
Bottom Ash Sluice ⑦
Economizer Ash ⑧
Scrubber Solids to Pond ⑨
Scrubber Liquid to Pond ⑩
Fly Ash and Flue Gas Through Stack ⑪

FIGURE 2-1

IN AND OUTGOING STREAMS AT THE

BOILER NO. 4 AND SCRUBBER SYSTEM AT STATION I

FIGURE 2-2: SCHEMATIC OF STATION I


CRUSHED COAL
COAL
SILO
PULVERIZER
①
②
BOTTOM ASH SLUICE WATER
330 MW BOILER
ECONOMIZER HOPPER
ECONOMIZER ASH
⑧
AIR PREHEATER
CAT WALK TO SAMPLING PLATFORM
⑪
32′
100′
FORCED DRAFT FAN
RECYCLE SLURRY
SCRUBBER
PRIMARY AIR FAN
(6,7)
③
WATER INTAKE
BOTTOM ASH TO POND
④
POND RETURN
(9,10)
SLURRY TO POND
⑤ LIME FEED

Sample Point 1: Coal

Coal samples were collected from pneumatic transfer lines transporting coal from four of the seven mills to the boiler. A cyclone sampler was used to collect a sample from one line every 15 minutes. The individual samples were stored in closed plastic containers and divided using riffle buckets into two samples for analysis at the end of the sampling period.

The flow rate of coal to each of the mills was recorded hourly in the control room. The average total coal feed to the mills was corrected for moisture content to yield a dry coal feed rate. This rate compared with the coal-burn requirement calculated from unit load, unit heat rate and coal heat value within 1%.

Sample Point 2: Bottom Ash Sluice Water Inlet

Bottom ash was sluiced continuously with water from the last settling pond in a series of two ponds. A sample from the point of intake was collected, acidified to prevent wall adsorption of trace constituents and stored in a polypropylene bottle for analysis. This sample is referred to as clear pond return.

The flow rate of bottom ash sluice water was determined from the power requirements of the centrifugal pump used to transport the water from the settling pond. The power was calculated from periodic readings of an ammeter and read directly from a wattmeter. The average of the two determinations of power were converted to flow rate from the pump curves provided by the manufacturer.

Sample Point 3: Cooling Tower Blowdown

A portion of the cooling tower blowdown is used as pump seal water, demister wash in the scrubbers and for induced draft-fan sprays. A sample was collected at the bottom of the cooling tower, acidified to prevent wall adsorption of trace constituents and stored in a polypropylene bottle for analysis.

The flow rate of cooling tower blowdown to the scrubbers was determined from the total dynamic head developed across the two pumps transporting the water stream. The pump heads were recorded hourly and converted to flow rates with pump curves provided by the manufacturer.

Sample Point 4: Scrubber Make-Up Water

The scrubber make-up water is identical to the bottom ash sluice water inlet since both come from the same settling pond intake. One sample was therefore collected and analyzed for both streams. This sample is referred to as clear pond return.

The flow rate of make-up water to each of the three scrubbers was monitored by flowmeters. Hourly readings were taken and the total averaged over the sampling period.

Sample Point 5: Lime

Samples of lime were collected hourly between the lime storage silo and the scrubber slurry make-up tanks. The individual samples were combined in a polypropylene container for a composite sample for analysis.

The lime feed rate to the scrubber system was calculated from a calcium material balance around the system.

Sample Point 6: Bottom Ash Solids

Samples of the bottom ash sluice stream were collected every 15 minutes at the point of discharge into the settling pond. The individual samples were combined in a plastic container, and the solids and liquid later separated by filtration.

The bottom ash production rate could not be directly measured due to the random variations in size distribution of the ash particulates and solids content of the stream which prevented the accurate determination of the solids content of the sluice stream. The bottom ash rate was calculated from a total ash balance. The total ash production was determined from the coal feed rate and ash content. The ash content of the scrubber solids was determined from the titanium analyses of the scrubber solids, economizer ash, and lime. See Appendix A for a detailed description of this calculation. The bottom ash is then the difference between the total coal ash and the sum of the ash in the scrubber solids, economizer ash, and fly ash leaving in the flue gas.

Sample Point 7: Bottom Ash Sluice Water Outlet

A portion of the filtrate collected during the separation of solids and liquids in the bottom ash sluice stream described above was acidified to prevent wall adsorption of trace components and stored in polyethylene containers for analysis.

The bottom ash sluice water outlet flow is equal to the inlet flow described above as Sample Point 2.

Sample Point 8: Scrubber Solids

Samples were collected at 30-minute intervals from the exit stream of the scrubber slurry discharge line to the first settling pond. The solids were separated by filtration and the individual samples combined to form a composite sample for analysis.

The discharge rate of solids from the scrubber system was determined from the average solids content of the discharge stream and the discharge rate of liquid from the scrubber system.

Sample Point 9: Scrubber Liquid

Following the collection of the scrubber slurry sample the solids were allowed to settle. A portion of the supernatant liquid was decanted, filtered to remove fine particulates, acidified to prevent wall adsorption, and stored in a polypropylene container for analysis.

The flow rate of liquid from the scrubber system was calculated from a total water balance around the scrubber system. The inlet water to the system consists of the scrubber make-up water, cooling tower blowdown, and water from the moisture content and combustion of coal. The outlet water streams include the moisture in the exiting flue gas and the water discharged as part of the scrubber slurry discharge. The scrubber liquid discharge rate is then the difference between the sum of the inlet streams and the moisture in the exiting flue gas.

Sample Point 10: Economizer Ash

The accumulation of ash in the economizer hopper during the sampling period was collected in two large plastic containers. Random cores of ash from the two containers were combined and divided using riffle buckets to provide a composite sample for analysis.

The accumulation rate of economizer ash was determined from the volumetric measurement of the accumulation during the sampling period and the packing density of the ash.

Sample Point 11: Flue Gas and Fly Ash

Samples of the flue gas and particulate matter exiting the stack were collected using a wet electrostatic precipitator (WEP) as a particulate collection device. This sampling device is described in detail in Appendix A. This method of collection permits sampling over extended periods at isokinetic conditions without plugging as occurs in a filter. Thus, a sufficient quantity of fly ash can be recovered to permit repeated analyses and problems of trace element contamination by a filter substrate are avoided. To confirm the comparability of this sampling approach with the filter technique recommended by EPA, an EPA filter was run in series with the WEP at Station III. A 125 mm class "A" Gelman glass fiber filter was used in a glass filter holder immediately after the WEP in the sampling train. The filter holder was heated to avoid condensation on the filter. The particulate matter collected by the filter during four WEP runs was equivalent to a grain loading of 0.0009 grains/scf. The inlet particulate loading to the WEP was 0.21 grains/scf, giving a collection efficiency of the WEP of 99+%.

Samples of the mercury vapor in the flue gas were collected by a gold amalgamation technique. The sulfur in the gas stream was collected as per EPA Method 6 by absorption in a hydrogen peroxide solution in a glass frit bubbler and determined as the sulfate. Orsat analysis of the flue gas for oxygen and carbon dioxide was performed to determine gas density as per EPA Method 3. Flue gas moisture content was determined using an efficient copper-tubing condenser immersed in an ice bath.

The veolocity profile in the stack was determined using an S-type pitot per EPA Method 2. Traverses were made over 20 points on each of two perpendicular diameters of the stack per EPA Method 1.

The average particulate loading was obtained from cumulative sampling with "in-stack" Gelman filter devices over the same set of sampling points. Four cumulative samples were required to cover the 40 points and the results of the four were averaged.

The WEP samples were collected at a single point in the stack and a correction made from this point to the average grain loading. The dust concentration at the sampling point was determined from the titanium concentration in the WEP sample assuming that titanium is evenly distributed in the particulates with respect to particle size. This assumption is based on work performed by Davison, et al. (DA-105) in which fly ash samples were collected from the duct of a coal-fired station. Andersen impactor samplers were used to separate the particulates into seven size fractions. The results of this work for titanium are presented in Table 2-1. It is evident from these data that the assumption of uniform as composition with respect to titanium holds within experimental limits.

The relationship between particle size and titanium concentration in the fly ash is important to this correction because the economizer ash has a larger average particle size than the exiting fly ash. If the titanium concentration were dependent on particle size, then the assumption made in Equation (2-1) that the titanium concentration in the fly ash is the same as in the economizer ash is invalid.

TABLE 2-1

TITANIUM ANALYSES* OF ANDERSEN IMPACTOR PARTICLE SIZE FRACTIONS (DA-105)

Particle Diameter µm	wt% Ti
>11.3	1.12
7.3 - 11.3	--
4.7 - 7.3	0.92
3.3 - 4.7	--
2.06 - 3.3	1.59
1.06 - 2.06	--
0.65 - 1.06	1.08

* Analysis by X-ray fluorescence spectrometry

The point grain loadings were determined from the titanium concentration in the WEP samples and the titanium weight fraction in the economizer ash using the relation:

$$\text{Point grain load (gr/scf)} = \frac{15.4\ V_L}{V_G}\ \frac{XW_L(Ti)}{XW_{Ash}(Ti)} \qquad (2\text{-}1)$$

where,

V_L = volume of the WEP liquor (ml)

V_G = volume of flue gas sampled by WEP (scf)

$XW_L(Ti)$ = concentration of Ti in the WEP liquor (μg/ml)

$XW_{Ash}(Ti)$ = weight fraction of Ti in the economizer ash (ppm)

The point to average grain loading correction factor is then the ratio of the average grain loading to the point grain load calculated from Equation (2-1). The correction factor was 1.4.

2.3 Summary of Flow Rates and Estimated Errors

A summary of the flow rates is given in Table 2-2. The error limits presented in this table are largely based on Radian field experience. The error limits presented for those flows calculated from material balances were calculated by propagation of analytical and flow rate error limits through the balance calculation. Also summarized in this table are the procedures used to obtain the listed rates.

TABLE 2-2

FLOW RATES FOR STREAMS AROUND STATION I

Stream	Flow Rate	Error Limit	Method Used For Flow Determination
Coal	2.83×10^5 lb/hr.	±10%	Control room print-out and heat balance
Bottom Ash Sluice Water Inlet	1.29×10^6 lb/hr.	±15%	Pump power consumption and pump curves
Cooling Tower Blowdown	4.39×10^5 lb/hr.	±15%	Pump heads and pump curves
Scrubber Make-up Water	4.00×10^6 lb/hr.	±10%	Flowmeters
Lime	4.78×10^3 lb/hr.	±15%	Calculated from calcium material balance
Bottom Ash	1.15×10^4 lb/hr.	±40%	Calculated from total ash balance
Bottom Ash Sluice Water Outlet	1.29×10^6 lb/hr.	±15%	Rate was set equal to inlet sluice water
Scrubber Solids	5.00×10^4 lb/hr.	±20%	Calculated from slurry solids content and flow rate of scrubber liquid
Scrubber Liquid	4.18×10^6 lb/hr.	±10%	Calculated from total water balance around scrubbers
Economizer Ash	2.63 lb/hr.	±10%	Measured directly by volume and known density
Flue Gas	5.01×10^7 scfh	±10%	Measured by stack traverses
Fly Ash	1.65×10^2 lb/hr.	±10%	Determined from cumulative grain loadings

2.4 Sampling Schedule

All of the streams around Unit No. 4 at Station I with the exception of the economizer ash were continuous with short residence times. The total accumulation of economizer ash during the sampling period was collected to provide a representative sample. Time phasing of sampling was therefore not necessary.

The samples and measurements described briefly in the preceding sections were taken during the period September 2nd, 3rd, and 4th according to the schedule shown in Figure 2-3. Those samples enclosed in parenthesis were analyzed, the rest were retained in reserve.

2.5 Sample Analysis

The techniques used for the quantitative determination of the elements of interest were based on:

(1) atomic absorption
(2) X-ray fluorescence
(3) ion selective electrodes
(4) fluorometry, and
(5) colorimetry

The methods are described in greater detail in Appendix B "Analytical Procedures".

Figures 2-4 through 2-7 summarize the dissolution and analytical methods used for trace element determination in coal samples, ash/sludge samples, lime/limestone samples, and WEP and aqueous samples.

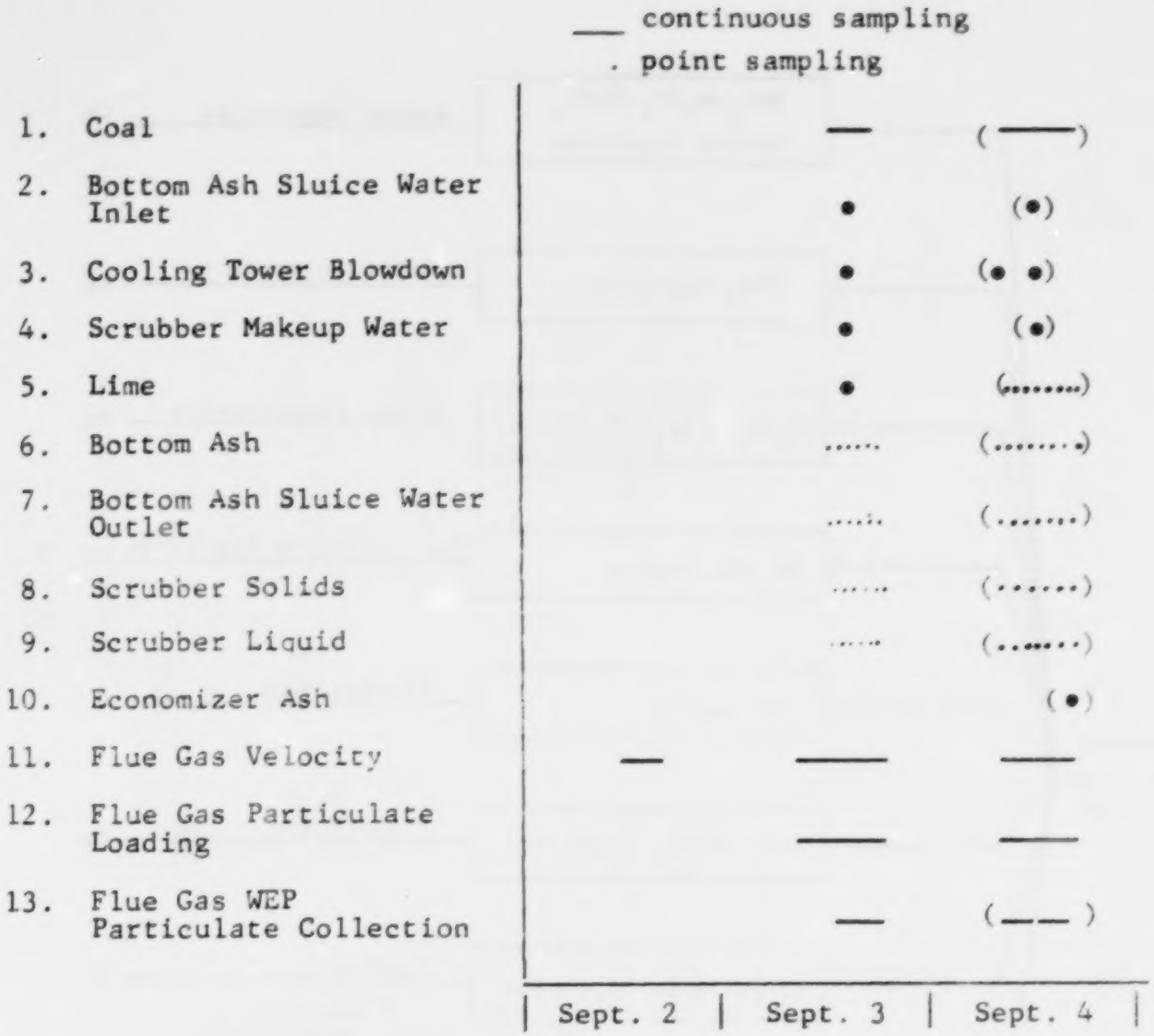


FIGURE 2-3

Sampling Schedule at Station I

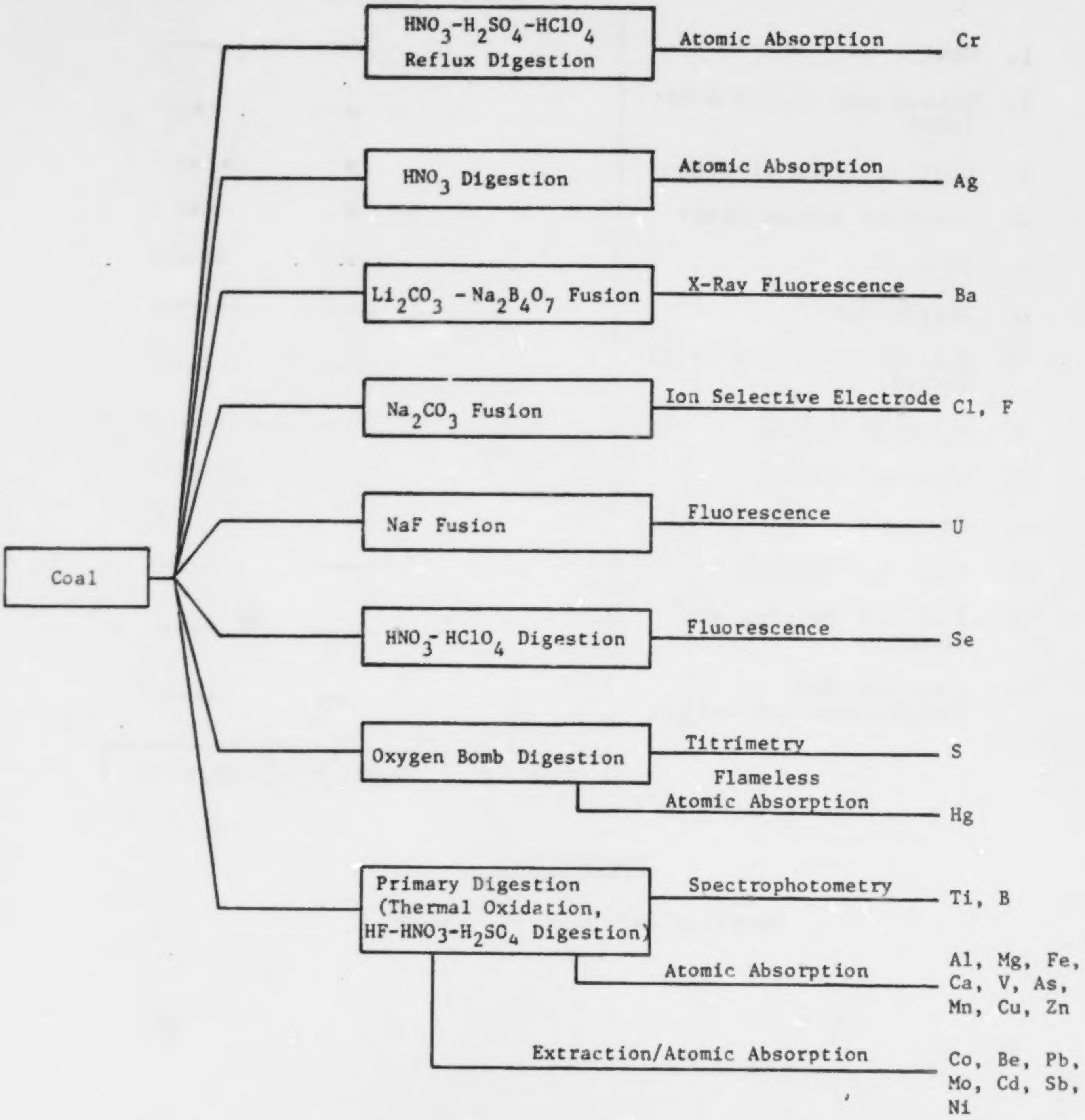

Coal
HNO_3-H_2SO_4-$HClO_4$ Reflux Digestion
Atomic Absorption
Cr
HNO_3 Digestion
Atomic Absorption
Ag
Li_2CO_3 - $Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
Na_2CO_3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO_3- $HClO_4$ Digestion
Fluorescence
Se
Oxygen Bomb Digestion
Titrimetry
S
Flameless Atomic Absorption
Hg
Primary Digestion (Thermal Oxidation, HF-HNO_3-H_2SO_4 Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni

FIGURE 2-1

ANALYSIS PROCEDURE FOR TRACE ELEMENT ANALYSIS
OF COAL

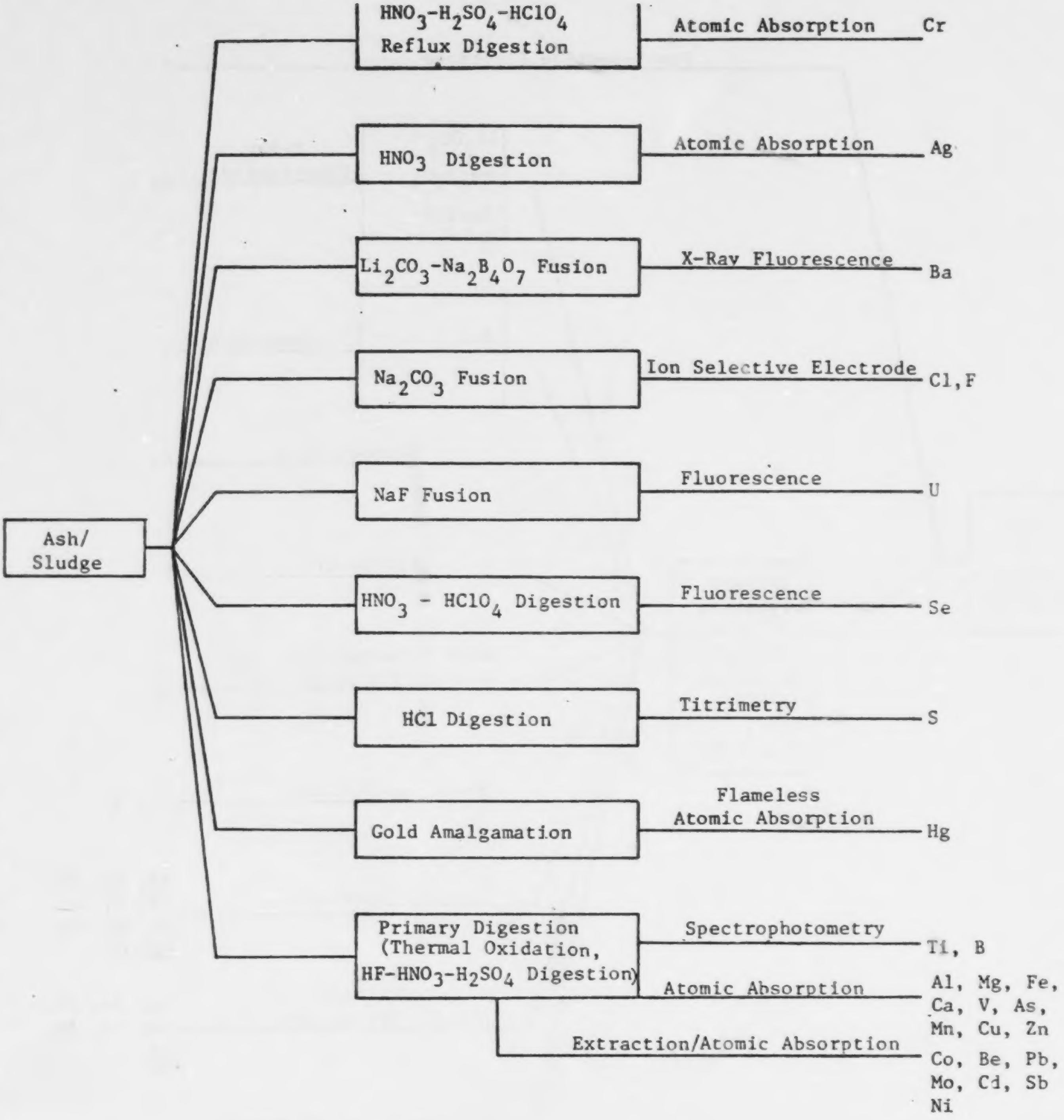

Ash/ Sludge
HNO_3-H_2SO_4-$HClO_4$ Reflux Digestion
Atomic Absorption
Cr
HNO_3 Digestion
Atomic Absorption
Ag
Li_2CO_3-$Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
Na_2CO_3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO_3 - $HClO_4$ Digestion
Fluorescence
Se
HCl Digestion
Titrimetry
S
Gold Amalgamation
Flameless Atomic Absorption
Hg
Primary Digestion (Thermal Oxidation, HF-HNO_3-H_2SO_4 Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb Ni

FIGURE 2-2

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS OF COAL ASH AND SLUDGE

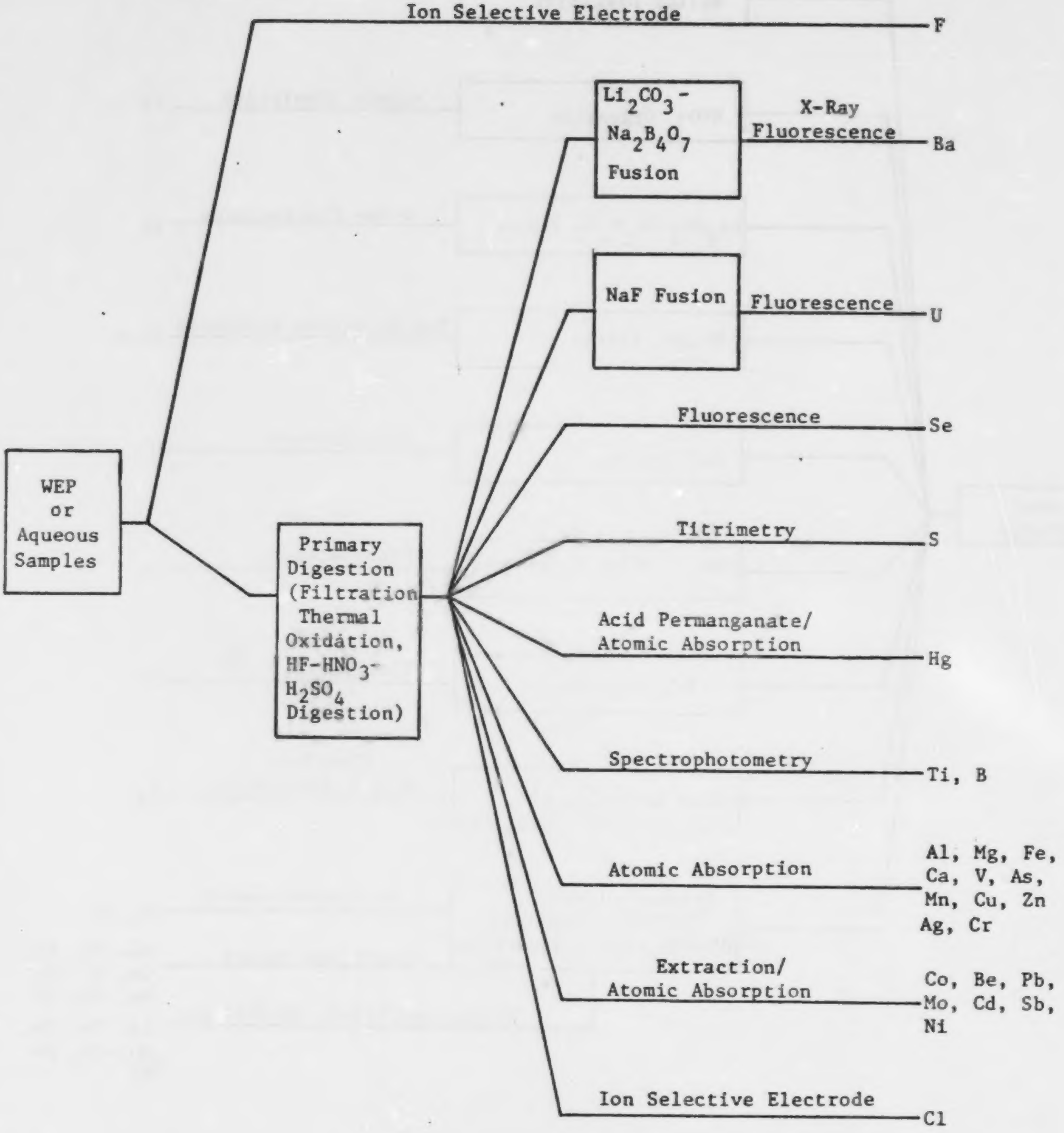

Ion Selective Electrode
F
Li_2CO_3-
$Na_2B_4O_7$
Fusion
X-Ray
Fluorescence
Ba
NaF Fusion
Fluorescence
U
Fluorescence
Se
WEP
or
Aqueous
Samples
Titrimetry
S
Primary
Digestion
(Filtration
Thermal
Oxidation,
HF-HNO_3-
H_2SO_4
Digestion)
Acid Permanganate/
Atomic Absorption
Hg
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe,
Ca, V, As,
Mn, Cu, Zn
Ag, Cr
Extraction/
Atomic Absorption
Co, Be, Pb,
Mo, Cd, Sb,
Ni
Ion Selective Electrode
Cl

FIGURE 2-4

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS
OF WET ELECTROSTATIC PRECIPITATOR LIQUORS AND AQUEOUS SAMPLES

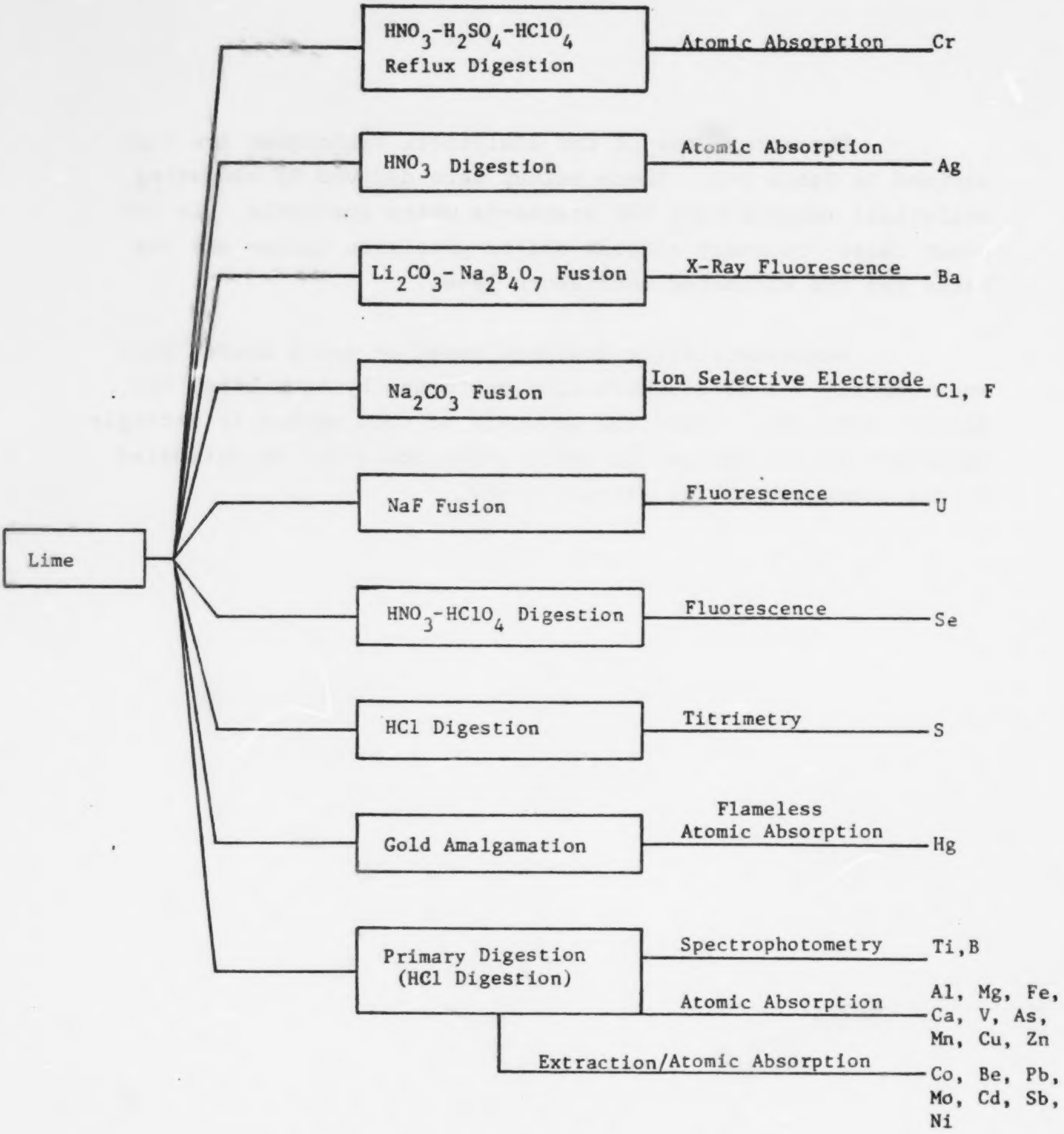

Lime
HNO_3-H_2SO_4-$HClO_4$ Reflux Digestion
Atomic Absorption
Cr
HNO_3 Digestion
Atomic Absorption
Ag
Li_2CO_3- $Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
Na_2CO_3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO_3-$HClO_4$ Digestion
Fluorescence
Se
HCl Digestion
Titrimetry
S
Gold Amalgamation
Flameless Atomic Absorption
Hg
Primary Digestion (HCl Digestion)
Spectrophotometry
Ti,B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni

FIGURE 2-3

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS OF LIME

The accuracies of the analytical techniques are summarized in Table 2-3. These values were derived by comparing analytical results with NBS standards where available. In the other cases, recovery studies and/or precision values are the basis for the estimated confidence level.

Semiquantitative analyses based on spark source mass spectrometry for 53 elements were performed by Accu-Labs, Inc, Denver, Colorado. Since the accuracy of this method is strongly dependent on the matrix, an error limit could not be estimated in the framework of the present study.

TABLE 2-3

ERROR LIMITS FOR THE CHEMICAL ANALYSES

	WEP Liquor	Aqueous Samples	Coal and Coal Ash	Lime	Scrubber Sludge
Aluminum	±10%	±10%	± 8%	± 8%	± 8%
Antimony	±10%	±10%	±15%	±12%	±12%
Arsenic*	± 8%	± 8%	±10%	±10%	±10%
Barium	±20%	±20%	±20%	±20%	±20%
Beryllium	±10%	±10%	±12%	±12%	±12%
Boron	± 8%	± 8%	± 8%	± 8%	± 8%
Cadmium*	±12%	±12%	±12%	±12%	±12%
Calcium	± 2%	± 2%	± 2%	± 2%	± 2%
Chlorine	±10%	±10%	± 8%	±10%	±10%
Chromium*	±10%	±10%	±12%	±12%	±12%
Cobalt	±10%	±12%	±10%	±12%	±12%
Copper*	±10%	±10%	±12%	±12%	±12%
Fluorine	± 8%	± 8%	± 8%	± 8%	± 8%
Iron*	± 6%	± 6%	± 6%	± 6%	± 6%
Lead*	±10%	±10%	±18%	±18%	±18%
Manganese*	±10%	±10%	± 8%	±10%	±10%
Magnesium	± 2%	± 2%	± 2%	± 2%	± 2%
Mercury*	±20%	±10%	±10%	±10%	±10%
Molybdenum	±12%	±12%	±15%	±15%	±15%
Nickel*	±12%	±12%	±12%	±18%	±18%
Selenium*	± 5%	± 5%	± 5%	± 7%	± 7%
Titanium	± 8%	± 8%	± 8%	± 8%	± 8%
Silver	±10%	±10%	±10%	±10%	±10%
Sulfur	±10%	± 2%	± 2%	± 2%	± 2%
Uranium*	± 8%	± 8%	± 6%	± 6%	± 6%
Vanadium*	±12%	±12%	±10%	±10%	±10%
Zinc*	±10%	±10%	±12%	±12%	±12%

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*By comparison with NBS Standard Reference Materials 1633 and 1634.

3.0 DATA EVALUATION

The flow rates and chemical analyses are used to calculate the transport rate of the elements of interest through the boiler and their discharge rates in the effluent streams. A material balance is made around the boiler for each of the elements to substantiate the individual measurements. The mathematical correlation forms are given in the next sections.

3.1 Trace Element Material Balances

The transport rates of the elements of interest through the steam station are calculated from the chemical analyses of the samples and the flow rates of the incoming and exiting streams. A material balance is calculated for each of the trace elements to verify the determined emission values.

Equating the trace element flow into the system to the flow out of the system gives the following expression:

$$\begin{aligned} & M_{c}XW_{c}(j) + M_{swi}Xw_{swi}(j) + M_{ctb}XW_{ctb}(j) + M_{mw}XW_{mw}(j) \\ & + M_{1}XW_{1}(j) = \qquad (3\text{-}1) \\ & M_{ba}XW_{ba}(j) + M_{swo}XW_{swo}(j) + M_{ss}XW_{ss}(j) + M_{s1}XW_{s1}(j) \\ & + M_{ea}XW_{ea}(j) + V_{fg}XV_{fg}(j) \end{aligned}$$

where,

M_c = the mass flow rate of coal into the boiler on a dry weight basis (lb/hr)

$XW_c(j)$ = the weight fraction of the element j in the coal on a dry weight basis

M_{swi} = the mass flow rate of bottom ash sluice water into the ash sluice system (lb/hr)

$XW_{swi}(j)$ = the weight fraction of the element j in the inlet bottom ash sluice water which is the same as clear pond return

M_{ctb} = the mass flow rate of cooling tower blowdown to the scrubber system (lb/hr)

$XW_{ctb}(j)$ = the weight fraction of the element j in the cooling tower blowdown

M_{mw} = the mass flow rate of the make-up water from the settling pond to the scrubber system (lb/hr)

$XW_{mw}(j)$ = the weight fraction of the element j in the make-up water to the scrubber system which is the same as clear pond return

M_l = the mass flow rate of lime into the scrubber system (lb/hr)

$XW_l(j)$ = the weight fraction of the element j in the lime

M_{ba} = the discharge rate of bottom ash from the boiler (lb/hr)

$XW_{ba}(j)$ = the weight fraction of the element j in the bottom ash

M_{swo} = the mass flow rate of the bottom ash sluice water from the sluice system which is equal to M_{swi} (lb/hr)

$XW_{swo}(j)$ = the weight fraction of the element j in the outlet bottom ash sluice water

M_{ss} = the discharge rate of solids from the scrubber system (lb/hr)

$XW_{ss}(j)$ = the weight fraction of the element j in the scrubber discharge solids

M_{sl} = the discharge rate of liquid from the scrubber system (lb/hr)

$XW_{sl}(j)$ = the weight fraction of the element j in the scrubber discharge liquid

M_{ea} = the discharge rate of economizer ash (lb/hr)

$XW_{ea}(j)$ = the weight fraction of the element j in the economizer ash

V_{fg} = the volumetric flow rate of the flue gas in the stack (scfh)

$XV_{fg}(j)$ = the weight of element j per unit volume of flue gas (lb/scf)

3.2 Error Propagation Analysis

An error propagation analysis was performed on the material balance equations for each element. Error limits are calculated for the total inlet and outlet rates of each element indicating the magnitude of variation to be expected due simply to random measuring errors.

Only errors random in nature are considered in this treatment. A variance is calculated for a given value according to the following standard definition.

$$S^2(Q) = \sum_i^n \left(\frac{\partial Q}{\partial q_i}\right)^2 S^2(q_i) \qquad (3\text{-}2)$$

where,

S(Q) = the variance in Q

Q = the material balance value which is a function of the q_i's

q_i = the $i^{\underline{th}}$ independent flow rate or composition used to calculate Q.

Confidence intervals can then be assigned to the trace element flow rates calculated for the various streams based on the errors associated with each measurement used in the calculation of these quantities. These limits will be included with the calculated rates discussed in the following section. The error limits for the flow rates were given in Table 2-2 and those assigned to the chemical analyses are listed in Table 2-3 and are in both cases as 2S.

4.0 RESULTS

The values for the proximate and ultimate analysis of the coal are presented in Table 4-1, the coal ash analysis in Table 4-2.

The quantitative analysis results are listed in Table 4-3. The element concentrations in the coal and the flow rates are reported on a dry weight basis. Most of the values in Table 4-3 are presented in parts per million on a dry weight basis for the solid samples or micrograms per milliliter for liquids. Some elements present in higher concentrations are listed as percent. The WEP results are presented in pounds per standard cubic foot of dry flue gas, where standard conditions are a temperature of 60°F and pressure of 29.92 inches of mercury.

Table 4-4 presents the analytical results obtained by SSMS. The economizer ash sample was analyzed in duplicate to estimate the precision of this method of analysis. Blind duplicates were also submitted for the WEP sample. The differences between duplicates were large for some of the elements as evidence by a factor of 6 for Ge, 5 for Nd, 5 for Sn, and 270 for Zn. However, these data (SSMS) are useful for order-of-magnitude estimates of trace element flows.

The trace element flow rates in lb/hr are listed in Table 4-5, using the quantitative analysis methods and in Table 4-6, using the SSMS results. The sum of the elemental flow rates of all incoming streams, coal and ash sluice water, are given

TABLE 4-1
STATION I COAL ANALYSIS

Proximate		As Received	Dry
% Moisture		26.95	0.00
% Ash		15.06	20.62
% Volatile Matter		31.13	42.61
% Fixed Carbon		26.86	36.77
	Total	100.00	100.00
% Sulfur		0.52	0.72
BTU/lb		6948	9511
Moisture and Ash Free BTU/lb	11,982		

Ultimate		As Received	Dry
% Carbon		42.00	57.48
% Hydrogen		6.87	4.49
% Nitrogen		0.47	0.65
% Oxygen		35.08	16.04
% Sulfur		0.52	0.72
% Ash		15.06	20.62
	Total	100.00	100.00

TABLE 4-2
STATION I ASH ANALYSIS

Mineral Analysis of Ash	Percent
Silicon Dioxide, SiO_2	50.10
Aluminum Oxide, Al_2O_3	20.29
Titanium Dioxide, TiO_2	0.77
Iron Oxide, Fe_2O_3	3.69
Sodium Oxide, Na_2O	0.15
Potassium Oxide, K_2O	1.31
Calcium Oxide, CaO	12.98
Magnesium Oxide, MgO	2.11
Phosphorus Pentoxide, P_2O_5	0.23
Sulfur Trioxide, SO_3	5.23
Other	3.14
Total	100.00

Ash Viscosity Calculations	
Basic Content (percent)	22.14
Acidic Content (percent)	77.86
Base-to-Acid Ratio	0.28
Silica-to-Alumina Ratio	2.47
Temperature for 250 Poise Viscosity, °F	2580

TABLE 4-3
ANALYTICAL RESULTS OF THE STATION I SAMPLES[1]

Element	Coal	Clear Pond Return	Cooling Tower Blowdown	Lime	Bottom Ash	Bottom Ash Sluice Water	Scrubber Slurry Solids	Scrubber Slurry Liquid	Economizer Ash	Combined WEP
Aluminum	2.3%	5.0	2.2	.30%	10.3%	2.4	10.8%	4.8	10.0%	20.
Antimony	.53	.024	.024	<.6	.39	.041	2.3	.036	2.1	<.002
Arsenic	.83	.0045	.003	<.06	1.3	.0041	5.2	.0013	3.3	.026
Barium	130.	<.5	<.5	<40.	670.	<.5	840.	<.5	800.	<.5
Beryllium	.82	.0013	.0036	1.2	2.5	.0013	3.2	.0015	3.2	.0014
Boron	51.	3.2	.27	6.8	160.	2.5	220.	2.8	260.	.81
Cadmium	.18	.0054	.001	.46	1.0	.0038	1.8	.0068	7.3	.0095
Calcium	1.76%	790.	140.	53.5%	8.66%	790.	11.8%	910.	11.5%	68.
Chlorine	44.	28.	25.	125.	140.	28.	89.	28.	200.	22.
Chromium	21.	.074	< .056	12.	67.	.12	118.	.14	.114	.92
Cobalt	2.1	.0081	.026	1.4	7.0	.005	8.1	.011	15.	.016
Copper	34.	.036	.24	17.	93.	.024	155.	.049	105.	.07
Fluorine	140.	20.	.91	520.	100.	16.	820.	20.	120.	1.2[2]
Iron	.40%	.31	1.2	.12%	2.51%	.30	2.25%	.74	2.15%	10.
Lead	4.2	.008	.016	11.	7.1	.007	49.	.023	15.	.061
Manganese	170.	.86	.10	77.	690.	.79	.10%	.88	.10%	.27
Magnesium	.29%	68.	37.	.46%	1.20%	68.	1.36%	62.	1.47%	11.
Mercury	.13	<.0005	<.0004	.057	.014	<.0005	.053	.0007	<.010	.004
Molybdenum	4.0	.035	.05	4.5	3.7	.056	10.	.015	34.	.43
Nickel	9.0	.025	.005	3.3	39.	.015	38.	.015	47.	.12
Selenium	2.2	.048	.0037	.27	.70	.031	8.7	.12	.46	.020
Titanium	.11%	<.1	<.1	87.	.45%	<.1	.40%	<.1	.48%	.96
Silver	.045	.0003	.0003	< .013	.11	0004	.23	.0005	.093	.0008
Sulfur	.72%	785.	.27%	29.	.11	770.	1.44%	865.	.30	2370
Uranium	1.3	.010	.015	7.8	13.	.0058	3.6	.0087	7.6	.0069
Vanadium	51.	.16	.14	31.	230.	.19	268.	.23	275.	.50
Zinc	24.	.10	.40	6.3	41.	.076	190.	.089	57.	.30

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[1] Values represent the average of duplicate determinations. Values for liquid samples are reported as ug/ml and solids samples as ppm on a dry basis, unless otherwise noted. WEP analysis in 10^{-8} lb/scf (60°F, 29.92" Hg).

[2] Analysis from reserve WEP (529).

TABLE 4-4 STATION I, ANALYTICAL RESULTS BY SS-MS[1]

Element	Coal	Clear Pond Return	Cooling Tower Blowdown	Lime	Bottom Ash	Bottom Ash Sluice Water	Scrubber Slurry Solids	Scrubber Slurry Liquid	Economizer Ash[2]		Flue Gas WEP[2]	
Aluminum	28600	2.1	.44	77	> 1%	13	>1%	4.1	>.5%	>1%	11	2.8
Antimony	.43	.011	--	< .06	.49	.021	.82	.016	1.2	.53	.012	.0016
Arsenic	1.3	< .005	< .001	< .71	5.4	< .003	17	.002	10	6	.0098	.0098
Barium	130	.15	.067	6.9	320	.34	110	.22	100	130	.16	.15
Beryllium	1.9	--	--	.28	11	--	7.5	--	5.6	5.6	.16	.15
Bismuth	< .70	--	--	< .10	.21	--	.46	--	.35	.74	<.0016	<.0016
Boron	110	< .1[4]	.2[4]	1.4	800	< .1[4]	530	< .1[4]	500	500	.0016	<.0016
Bromine	1.7	.026	--	.22	1.5	.055	.98	.018	1.6	1.6	<.16[4]	<.16[4]
Cadmium	.62	.048	.13	.18	.67	.15	.89	.048	3.3	1.4	<.0016	<.0016
Calcium	>1%	740	110	>1%	>1%	720	>1%	840	>1%	>1%	.31	.033
Cerium	56	.006	--	10	200	.003	100	.004	100	35	66	68
Cesium	.66	.002	.005	.01	4.3	.005	2.8	.001	2.1	2.1	.026	.026
Chlorine	100	.018[3]	.003[3]	13	26	.28[3]	17	.093[3]	9.8	5.6	.012	.053
Chromium	29	.004	.002	.57	110	.002	180	.004	160	57	.016[3]	.0032[3]
Cobalt	5.9	.023	.041	.37	26	.010	17	.014	20	13	1.2	.51
Copper	25	.052	.13	1.2	120	.14	340	.18	120	60	.051	.046
Dysprosium	1.6	--	--	.21	4.2	--	2.8	--	4.2	2.1	.15	.068
											<.0016	<.0016

NOTES: [1] Concentration in ppm by weight in solids and μg/ml in liquids. WEP analysis in 10^{-6} lb/scf (60°F, 29.92" Hg).
[2] Blind duplicate analysis.
[3] Possibly inaccurate due to loss from acidic solution.
[4] Approximate value only due to interference from preservative.
[5] Insufficient sample for determination.
--All elements not reported <0.1 ppm weight in solids or <0.001 μg/ml in liquids.
Maj. - Major component.

TABLE 4-4 STATION I, ANALYTICAL RESULTS BY SS-MS^{1} (Cont'd)

Element	Coal	Clear Pond Return	Cooling Tower Blowdown	Lime	Bottom Ash	Bottom Ash Sluice Water	Scrubber Slurry Solids	Scrubber Slurry Liquid	Economizer Ash^{2}		Flue Gas WEP^{2}	
Erbium	.51	--	--	.07	.48	--	.48	--	.51	.51	<.0016	<.0016
Europium	.83	--	--	.07	1	--	.69	--	1.2	1.2	<.0016	<.0016
Fluorine	330	2.2^{3}	^{3}	450	91	^{3}	300	.81^{3}	80	120	.0065^{3}	^{5}
Gadolinium	.13	--	.003	.08	.69	--	1.1	--	.34	.90	<.0016	.0032
Gallium	3.7	.014	.003	.67	27	.006	48	.045	13	13	.15	.069
Germanium	.57	.033	.001	.04	2.8	.069	4	.049	1.4	3	.018	.0032
Gold	--	--	--	--	--	--	--	--	--	--	<.0016	<.0016
Hafnium	.31	--	--	.67	5.7	--	1.8	--	2.9	2	<.0016	<.0016
Holmium	.15	--	--	.02	.31	--	.20	--	.27	.37	<.0016	<.0016
Iodine	1.2	--	--	.18	.60	.004	.20	.001	.15	.18	<.0016	<.0016
Iridium	--	--	--	--	--	--	--	--	--	--	<.0016	<.0016
Iron	>.5%	.46	1.1	~5700	>1%	1.2	>1%	.92	>1%	>1%	14	13
Lanthanum	9	.003	--	.87	31	.010	20	.003	24	15	.025	.023
Lead	2.9	.004	.005	< .10	8	.013	27	.003	8.5	8.6	.031	.028
Lithium	67	.029	.001	7.5	860	.13	2	.044	430	430	.013	<.0016
Lutetium	.08	--	--	.04	.15	--	.10	--	.11	.15	<.0016	<.0016
Magnesium	>1%	70	35	~5000	>1%	69	>1%	65	>1%	>1%	14	15
Manganese	80	.52	.037	170	~3300	.40	~2200	1	~3300	~3300	.36	.33
Mercury	.12^{3}	^{5}	^{5}	--	--	^{5}	--	^{5}	.03^{3}	--	<.0016	^{5}
Molybdenum	14	.066	.012	8.7	35	.14	23	.10	17	17	.069	.16

NOTES: [1] Concentration in ppm by weight in solids and μg/ml in liquids. WEP analysis in 10^{-9} lb/scf (60°F, 29.92" Hg).
[2] Blind duplicate analysis.
[3] Possibly inaccurate due to loss from acidic solution.
[4] Approximate value only due to interference from preservative.
[5] Insufficient sample for determination.
--All elements not reported <0.1 ppm weight in solids or <0.001 μg/ml in liquids.
Maj. - Major component.

TABLE 4-4 STATION I, ANALYTICAL RESULTS BY SS-MS[1] (Cont'd)

Element	Coal	Clear Pond Return	Cooling Tower Blowdown	Lime	Bottom Ash	Bottom Ash Sluice Water	Scrubber Slurry Solids	Scrubber Slurry Liquid	Economizer Ash [2]		Flue Gas WEP [2]	
Neodymium	75	.005	--	1.3	130	.011	84	.003	63	63	.053	.0098
Nickel	13	.46	.077	1.4	28	.077	19	.69	10	11	.69	.86
Niobium	5.4	--	--	.39	18	--	24	--	18	18	.016	.036
Osmium	--	--	--	--	--	--	--	--	--	--	<.0016	<.0016
Palladium	--	--	--	--	--	--	--	--	--	--	<.0016	<.0016
Phosphorus	640	.064	~.41	100	~1800	.11	1700	.097	~2400	~1800	8.1	~3.6
Platinum	--	--	--	--	--	--	--	--	--	--	<.0016	<.0016
Potassium	~2600	11	8.2	51	~2400	12	>.5%	12	1200	>.5%	4	4
Praseodymium	6 9	.001	--	.24	11	.001	7.6	--	5.7	5.7	.0016	.0049
Rhenium	--	--	--	--	--	--	--	--	--	--	<.0016	<.0016
Rhodium	--	--	--	--	--	--	--	--	--	--	<.0016	<.0016
Rubidium	9	.45	.041	.11	23	.089	32	.029	11	11	.10	.092
Ruthenium	--	--	--	--	--	--	--	--	--	--	<.0016	<.0016
Samarium	.33	--	--	.06	1.9	--	1.3	--	.97	.97	<.0016	<.0016
Scandium	13	--	--	1.7	80	--	53	--	40	40	<.0016	<.0016
Selenium	1.6	.15	.066	.22	.87	.19	5.8	.13	.22	.93	.46	.41
Silicon	>1%	Maj.	~2.5	~7800	>1%	Maj.	>1%	Maj.	>1%	>1%	Maj.	~56
Silver	.24	--	.008	.04	.14	.001	.19	.001	.10	.30	<.0016	<.0016
Sodium	510	76	86	240	~2200	78	>1%	80	~2400	>.5%	26	28
Strontium	150	6.6	.60	320	970	4.5	860	9.8	1400	~1400	1.5	1.8

NOTES: [1] Concentration in ppm by weight in solids and µg/ml in liquids. WEP analysis in 10^{-9} lb/scf (60°F, 29.92" Hg).

[2] Blind duplicate analysis.

[3] Possibly inaccurate due to loss from acidic solution.

[4] Approximate value only due to interference from preservative.

[5] Insufficient sample for determination.

--All elements not reported <0.1 ppm weight in solids or <0.001 µg/ml in liquids.

Maj. - Major component.

TABLE 4-4 STATION I, ANALYTICAL RESULTS BY SS-MS[1] (Cont'd)

Element	Coal	Clear Pond Return	Cooling Tower Blowdown	Lime	Bottom Ash	Bottom Ash Sluice Water	Scrubber Slurry Solids	Scrubber Slurry Liquid	Economizer Ash[2]		Flue Gas WEP[2]	
Sulfur	>1%	Maj.	Maj.	470	~9300	Maj.	>1%	Maj.	~9300	~9300	Maj.	~127
Tantalum	--	.007	--	.61	2.6	--	.80	.001	1.3	3	.0065	.0032
Tellurium	.10	--	--	< .07	.16	--	.09	.001	.07	< .07	<.0016	.0016
Terbium	.09	--	--	.02	.46	--	.15	--	.27	.11	<.0016	<.0016
Thallium	< .10	--	--	< .10	.19	--	.25	--	.28	.40	.012	<.0016
Thorium	2.6	--	--	.64	13	--	18	--	14	14	.0016	<.0016
Thulium	.04	--	--	.02	.26	--	.12	--	1.3	.13	<.0016	<.0016
Tin	1.8	.004	.007	.17	2	.004	3.1	.012	2.3	2.3	.18	.038
Titanium	~1900	.23	.075	57	>1%	--	>1%	.22	~8500	~6800	4.3	2.6
Tungsten	3.4	.005	--	1.1	3.7	.003	5	.003	8	6.2	.0049	.0098
Uranium	2.5	.002	--	1.2	23	.002	7.2	.003	5.4	12	.0049	.0098
Vanadium	73	.19	.006	1.3[3]	180	.067	280	.29	160	260	.89	.86
Ytterbium	.27	--	--	.15	1	--	1.4	--	.38	1.1	<.0016	<.0016
Yttrium	17	.001	--	2.1	75	.016	50	.002	110	58	.0082	.015
Zinc	.87	.10	.40	.21	10	.074	66	.051	27	18	.87	.0032
Zirconium	31	.003	--	1.1	62	.006	76	.004	57	57	.016	.028

NOTES: [1] Concentration in ppm by weight in solids and μg/ml in liquids. WEP analysis in 10^{-6} lb/scf (60°F, 29.92" Hg).
[2] Blind duplicate analysis.
[3] Possibly inaccurate due to loss from acidic solution.
[4] Approximate value only due to interference from preservative.
[5] Insufficient sample for determination.
--All elements not reported <0.1 ppm weight in solids or <0.001 μg/ml in liquids.
Maj. - Major component.

TABLE 4-5 STATION I MATERIAL BALANCES*

Element	Coal	Ash Sluice Water	Cooling Tower Blowdown	Make-Up Water	Lime	Σ In	Bottom Ash	Ash Sluice Water	Scrubber Solids	Scrubber Liquid	Economizer Ash	Flue Gas	Σ Out	Σ Out/Σ In
Aluminum	6509	6.5	1.0	20	14	6550 ± 830	1188	3	5400	20	2.6	16.5	6630 ± 1260	1.01
Antimony	.15	.03	.01	.096	.003	.29 ± .03	.0045	.053	.12	.15	.00005	.0017	.33 ± .04	1.14
Arsenic	.23	.0058	.0013	.018	.0003	.26 ± .03	.015	.0053	.26	.0054	.00008	.021	.31 ± .06	1.19
Barium	37	.63	.22	2	.19	40 ± 8	7.7	.65	42	2	.02	.41	53 ± 12	1.33
Beryllium	.23	.0017	.0016	.0052	.0057	.25 ± .03	.029	.0017	.16	.0063	.00008	.0012	.20 ± .04	.80
Boron	14	4.1	.12	13	.03	32 ± 3	1.8	3.2	11	12	.0068	.67	28 ± 3	.88
Cadmium	.051	.0070	.0004	.022	.0022	.082 ± .009	.012	.0049	.09	.028	.0002	.0078	.14 ± .02	1.71
Calcium	4980	1019	61	3160	2557	11,800 ± 700	995	1019	5900	3804	3	56	11,800 ± 1300	1.00
Chlorine	12	36	11	112	.60	170 ± 17	2	36	4	117	.005	18	180 ± 18	1.06
Chromium	5.9	.095	< .025	.30	.057	6.4 ± .8	.77	.15	5.9	.59	.0030	.76	8 ± 1	1.25
Cobalt	.59	.010	.011	.032	.0067	.66 ± .08	.081	.0065	.41	.046	.0004	.013	.6 ± .1	.91
Copper	9.6	.046	.11	.14	.081	10 ± 2	1.1	.031	7.8	.20	.0028	.058	9 ± 2	.90
Fluorine	40	26	.40	80	2	150 ± 12	1.2	21	41	84	.0032	.85	150 ± 14	1.00
Iron	1132	.4	.5	1	6	1140 ± 130	289	.4	1125	3	.6	9	1430 ± 260	1.25
Lead	1.2	.010	.007	.032	.053	1.3 ± .2	.082	.009	2.5	.096	.0004	.05	2.7 ± .7	2.08
Magnesium	821	88	16	272	22	1200 ± 90	138	88	680	259	.4	9	1170 ± 150	.98
Manganese	48	1.1	.044	3.4	.37	53 ± 6	8.0	1.0	50	3.7	.026	.22	60 ± 10	1.13
Mercury	.037	.0006	.0002	.002	.0003	.040 ± .005	.0002	.0006	.0027	.0029	2×10^{-7}	.022	.029 ± .004	.73
Molybdenum	1.1	.045	.022	.14	.022	1.4 ± .2	.043	.072	.52	.063	.0009	.36	1.1 ± .1	.79
Nickel	2.5	.032	.002	.10	.016	2.7 ± .4	.45	.019	1.9	.068	.001	.099	2.5 ± .5	.93
Selenium	.62	.062	.0016	.19	.0013	.88 ± .07	.008	.040	.44	.50	.00001	.017	1.0 ± .1	1.14
Silver	.013	.0004	.0001	.0012	.00006	.014 ± .002	.0013	.0005	.012	.002	2×10^{-6}	.0007	.016 ± .003	1.14
Sulfur	2038	1013	1185	3140	.14	7380 ± 410	.001	993	720	3615	7×10^{-6}	1185	6510 ± 440	.88
Titanium	311	<.13	<.04	<.4	.42	310 ± 40	52	<.13	200	<.4	.13	.79	250 ± 50	.81
Uranium	.37	.013	.0066	.04	.037	.46 ± .04	.15	.007	.18	.036	.0002	.0057	.38 ± .07	.83
Vanadium	14	.20	.062	.63	.15	15 ± 2	2.6	.25	13	.97	.007	.41	18 ± 3	1.20
Zinc	6.8	.13	.18	.40	.030	8 ± 1	.47	.098	9.5	.37	.0015	.25	11 ± 2	1.38

* All values in lb/hr.

TABLE 4-6 TRACE ELEMENT FLOWS* AND MATERIAL BALANCE RESULTS AROUND STATION I FROM SPARK SOURCE MASS SPECTROMETRY ANALYSES

Element	Coal	Bottom Ash Sluice Water	Cooling Tower Blowdown	Make-up Water	Lime	Σ In	Bottom Ash	Bottom Ash Sluice Water	Scrubber Solids	Scrubber Liquid	Economizer Ash	Flue Gas	Σ Out
Aluminum	~2434	2.7	.19	8.4	.37	~2400	>115	17	>500	17	>.26	3.5	>650
Antimony	.12	.014	< .0004	.044	< .0002	.18	.006	.027	.041	.067	.00002	.003	.14
Arsenic	.37	< .006	< .0004	< .02	< .003	.40	.062	< .004	.85	.008	.0002	.005	.93
Barium	37	.19	.029	.60	.033	38	3.7	.44	5.5	.92	.003	.079	11
Beryllium	.54	< .001	< .0004	< .004	.001	.54	.13	< .001	.38	< .004	.0001	< .0008	.51
Bismuth	< .20	< .001	< .0004	< .004	< .0004	< .20	.002	< .001	.023	< .004	.00001	.0008	.032
Boron	31	< .13	.088	< .40	.007	32	9.2	< .13	27	< .42	.013	< .083	36
Bromine	.48	.034	< .0004	.10	.001	.62	.017	.071	.049	.075	.00004	< .0008	.21
Cadmium	.18	.062	.057	.19	.0008	.49	.008	.19	.045	.20	.00006	.091	.54
Calcium	>2830	955	48	2960	>48	>6800	>115	929	>500	3511	>.26	34	>5100
Cerium	16	.008	< .0004	.024	.049	16	2.3	.004	5	.017	.002	.013	7.3
Cesium	.19	.003	.002	.008	.00004	.20	.049	.006	.14	.004	.00005	.017	.22
Chlorine	28	.023	.001	.072	.062	28	.30	.36	.85	.39	.0002	.005	1.9
Chromium	8.2	.005	.0008	.016	.003	8.2	1.3	.003	9	.017	.003	.42	11
Cobalt	1.7	.030	.018	.092	.002	1.8	.30	.013	.85	.059	.0004	.025	1.2
Copper	7.1	.067	.057	.21	.006	7.4	1.4	.18	17	.75	.002	.055	19
Dysprosium	.45	< .001	< .0004	< .004	.001	.46	.048	< .001	.14	< .004	.00008	< .0008	.19
Erbium	.14	< .001	< .0004	< .004	.0003	.15	.006	< .001	.024	< .004	.00001	< .0008	< .036
Europium	.23	< .001	< .0004	< .004	.0003	.24	.012	< .001	.035	< .004	.00003	< .0008	.052
Fluorine	93	2.8	--	8.8	2.1	110	1.0	--	15	3.4	.003	.003	19
Cadolinium	.037	< .001	.001	< .004	.0003	< .044	.008	< .001	.055	< .004	.00001	.002	.070
Gallium	1.0	.018	.001	.056	.003	1.1	.31	.008	2.4	.19	.0003	.056	3.0
Germanium	.16	.043	.0004	.13	.0001	.34	.032	.089	.20	.20	.00005	.006	.53
Gold	< .028	< .001	< .0004	< .004	< .0004	< .034	< .001	< .001	< .005	< .004	$< 2 \times 10^{-6}$	< .0008	< .012
Hafnium	.088	< .001	< .0004	< .004	.003	.096	.066	< .001	.090	< .004	.00006	< .0008	.16
Holmium	.042	< .001	< .0004	< .004	.00009	< .048	.004	< .001	.01	< .004	8×10^{-6}	< .0008	< .020

*All flows in lb/hr.

TABLE 4-6 TRACE ELEMENT FLOWS* AND MATERIAL BALANCE RESULTS AROUND STATION I FROM SPARK SOURCE MASS SPECTROMETRY ANALYSES (Co

Element	Coal	Bottom Ash Sluice Water	Cooling Tower Blowdown	Make-up Water	Lime	Σ In	Bottom Ash	Bottom Ash Sluice Water	Scrubber Solids	Scrubber Liquid	Economizer Ash	Flue Gas	Σ Out
Iodine	.34	< .001	< .0004	< .004	.0008	.35	.007	.005	.01	.004	4×10^{-6}	< .0008	.027
Iridium	< .028	< .001	< .0004	< .004	< .0004	< .034	< .001	< .001	< .005	< .004	$< 2 \times 10^{-6}$	< .0008	< .012
Iron	>1415	.59	.48	1.8	~27	>1400	>115	1.5	>500	3.8	>.26	6.7	>630
Lanthanum	2.5	.004	< .0004	.012	.004	2.6	.36	.013	1.0	.013	.0005	.012	1.4
Lead	.82	.005	.002	.016	< .0004	.84	.092	.017	1.4	.013	.0002	.015	1.5
Lithium	19	.037	.0004	.62	.036	19	9.9	.17	.10	.18	.011	.007	10
Lutetium	.023	< .001	< .0004	< .004	.0001	< .029	.002	< .001	.005	< .004	3×10^{-6}	< .0008	< .013
Magnesium	>2800	90	15	280	~24	>3200	>115	89	>500	272	>.26	7.3	>980
Manganese	23	.67	.016	2.1	.81	26	~38	.52	~110	4.2	~.087	.17	~153
Mercury	.034	--	--	--	< .0004	.034	< .001	--	< .005	--	7×10^{-7}	--	< .006
Molybdenum	4.0	.085	.005	.26	.042	4.4	.40	.18	1.2	.42	.0004	.057	2.2
Neodymium	21	.006	< .0004	.02	.006	21	1.5	.014	4.2	.013	.002	.016	5.7
Nickel	3.7	.59	.034	1.8	.007	6.2	.32	.099	.95	2.9	.0002	.39	4.6
Niobium	1.5	< .001	< .0004	< .004	.002	1.5	.21	< .001	1.2	< .004	.0004	.013	1.4
Osmium	< .028	< .001	< .0004	< .004	< .0004	< .034	< .001	< .001	< .005	< .004	$< 2 \times 10^{-6}$	< .0008	< .012
Palladium	< .028	< .001	< .0004	< .004	< .0004	< .034	< .001	< .001	< .005	< .004	$< 2 \times 10^{-6}$	< .0008	< .012
Phosphorus	181	.083	~.18	.26	.48	182	~21	.14	85	.41	.055	3.8	~110
Platinum	< .028	< .001	< .0004	< .004	< .0004	< .034	< .001	< .001	< .005	< .004	$< 2 \times 10^{-6}$	< .0008	< .012
Potassium,	~736	14	3.6	44	.24	~800	~28	15	>250	50	>.13	2	>350
Praseodymium	2.0	.001	< .0004	.004	.001	2.0	.13	.001	.38	< .004	.0001	.002	.51
Rhenium	< .028	< .001	< .0004	< .004	< .0004	< .034	< .001	< .001	< .005	< .004	$< 2 \times 10^{-6}$	< .0008	< .012
Rhodium	< .028	< .001	< .0004	< .004	< .0004	< .034	< .001	< .001	< .005	< .004	$< 2 \times 10^{-6}$	< .0008	< .012
Rubidium	2.5	.58	.018	1.8	.0005	4.9	.26	.11	1.6	.12	.0002	.050	2.2
Ruthenium	< .028	< .001	< .0004	< .004	< .0004	< .034	< .001	< .001	< .005	< .004	$< 2 \times 10^{-6}$	< .0008	< .012

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*All flows in lb/hr.

TABLE 4-6 TRACE ELEMENT FLOWS* AND MATERIAL BALANCE RESULTS AROUND STATION I FROM SPARK SOURCE MASS SPECTROMETRY ANALYSES (Cont'

Element	Coal	Bottom Ash Sluice Water	Cooling Tower Blowdown	Make-up Water	Lime	Σ In	Bottom Ash	Bottom Ash Sluice Water	Scrubber Solids	Scrubber Liquid	Economizer Ash	Flue Gas	Σ Ou
Samarium	.093	< .001	<.0004	< .004	.0002	.099	.022	< .001	.065	< .004	.00002	< .0008	.093
Scandium	3.7	< .001	< .0004	< .004	.008	3.7	.92	< .001	2.7	< .004	.001	< .0008	3.6
Selenium	.45	.19	.029	.60	.001	1.3	.010	.25	.29	.54	.00001	.22	1.3
Silver	.068	< .001	.004	< .004	.0001	.077	.002	.001	.010	.004	5 x 10^{-6}	< .0008	.017
Sodium	144	98	38	304	1.1	590	∼25	101	>500	334	>.13	14	>974
Strontium	42	8.5	.26	26	1.5	79	11	5.8	43	41	.037	.83	102
Tantalum	< .028	.009	< .0004	.028	.003	< .068	.030	< .001	.04	.004	.00005	.002	.078
Tellurium	.028	< .001	< .0004	< .004	< .0003	< .034	.002	< .001	.005	.004	1 x 10^{-6}	.0008	.013
Terbium	.025	< .001	< .0004	< .004	.00009	< .031	.005	< .001	.008	< .004	4 x 10^{-6}	< .0008	< .019
Thallium	< .028	< .001	< .0004	< .004	< .0004	< .034	.002	< .001	.013	< .004	.000008	.006	.026
Thorium	.74	< .001	< .0004	< .004	.003	.74	.15	< .001	.90	< .004	.0003	.0008	1.1
Thulium	.011	< .001	< .0004	< .004	.00009	< .017	.003	< .001	.006	< .004	.00001	< .0008	< .015
Tin	.51	.005	.003	.016	.0008	.53	.023	.005	.16	.050	.00006	.055	.29
Titanium	∼538	.30	.033	.92	.27	∼540	115	< .001	>500	.92	∼.20	1.7	>620
Tungsten	.96	.006	< .0004	.02	.005	.99	.042	.004	.25	.013	.0001	.004	.31
Uranium	.71	.003	< .0004	.008	.006	.72	.26	.003	.36	.013	.0002	.004	.64
Vanadium	21	.25	.003	.76	.006	22	>2.1	.086	14	1.2	.005	.44	18
Ytterbium	.076	< .001	< .0004	< .004	.0007	< .083	.012	< .001	.07	< .004	.00001	< .0008	.088
Yttrium	4.8	.001	< .0004	.004	.010	4.8	.86	.021	2.5	.008	.002	.006	3.4
Zinc	.25	.13	.18	.40	.001	.95	.12	.095	3.3	.21	.0006	.22	3.9
Zirconium	8.8	.004	< .0004	.012	.005	8.8	.71	.008	3.8	.017	.001	.012	4.6

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*All flows in lb/hr.

as Σ In. The elemental flow rates in the outgoing streams, bottom ash, bottom ash sluice water, scrubber solid and liquid discharge, economizer ash and flue gas, also were added and are listed as Σ Out. The error limits given were calculated from the estimated errors in the analyses and the estimated errors in the flows according to the procedures described in Section 3.0.

The emissions results for sulfur and particulates are summarized in Table 4-7 since these are the two emission parameters of greatest immediate importance. The results are provided on a lb/BTU basis to facilitate comparison to other stations.

TABLE 4-7

EMISSION RESULTS FOR PARTICULATES AND SULFUR DIOXIDE AT STATION I

	Particulates (Ash)	Sulfur Dioxide
Concentration in flue gas	.023 gr/scf	280 ppm (v/v)
Quantity in coal per unit heat value	21.7 lb/10^6 BTU	1.51 lb/10^6 BTU
Emissions in flue gas per unit heat value of coal burned	.061 lb/10^6 BTU	.88 lb/10^6 BTU

5.0 DISCUSSION OF RESULTS

The distribution of trace elements in station exit streams is affected by the properties of individual elements, the boiler configuration on the flue gas emission controls. The ability to distinguish the distribution patterns is dependent on the overall quality of the results. The criteria for acceptability of the trace element flow data used in this section is the degree of closure of individual element material balances.

5.1 Material Balance Closure

Closure of the balances within the error limits indicates a high degree of confidence of the individual trace element flows. Closure within the error limits is indicated by an overlap of the error bands for Σ In and Σ Out presented in Table 4-5. Twenty-four out of twenty-seven elemental material balances close within the error limits. These elements are:

Aluminum
Antimony
Arsenic
Barium
Beryllium
Boron
Calcium
Chlorine
Chromium
Cobalt
Copper
Fluorine
Iron
Magnesium
Manganese
Molybdenum
Nickel
Selenium
Silver
Sulfur
Titanium
Uranium
Vanadium
Zinc

The balances are out of limits for:

Cadmium	0.082 ± .009 lb/hr in	.14 ± .02 lb/hr out
Lead	1.3 ± .2 lb/hr in	2.7 ± .7 lb/hr out
Mercury	0.040 ± .005 lb/hr in	.029 ± .004 lb/hr out

This must be attributed to inaccuracies in sampling, sample handling and/or sample analysis particularly mercury which is in the gas phase in the flue gas making collection and analysis difficult. Normalized deviations in the material balances

$$ND(j) = \frac{\Sigma in(j) - \Sigma out(j)}{\{\Sigma in(j) + \Sigma out(j)\}/2} \qquad (5\text{-}1)$$

were calculated using Equation 5-1 for the results obtained from the quantitative analyses and by spark source mass spectrometry. The results are given in Table 5-1. The average of the normalized deviations were -0.06 and 0.26 for the quantitative methods and for SSMS respectively. These provide some measure of the overall material balance closure for each of the two analytical approaches.

The root mean square of the normalized deviations calculated by Equation (5-2) is 0.24 for the quantitative methods and 0.86 for the SSMS results.

$$RMS_{ND} = \left[\frac{1}{n} \sum_{j} \left(\frac{\Sigma in(j) - \Sigma out(j)}{\frac{\Sigma in(j) + \Sigma out(j)}{2}} \right)^2 \right]^{\frac{1}{2}} \qquad (5\text{-}2)$$

The same calculations for 48 elements analyzed by SSMS resulted in an average for the normalized deviations of 0.31 and a RMS value of 0.82. Analytical results less than or greater than a certain value were considered inconclusive and therefore not included in the latter calculations.

5.2 Distribution of Elements in the Exit Streams

The elements entering the station with the coal stream are distributed in the various ashes according to the individual element properties.

TABLE 5-1

DEVIATIONS FROM MATERIAL BALANCE CLOSURE FOR QUANTITATIVE ANALYSES AND SPARK SOURCE MASS SPECTROMETRIC ANALYSES FOR STATION I

Elements	Quantitative Normalized[1] Deviation	SSMS Normalized[1] Deviation
Aluminum	-0.01	1.15
Antimony	-0.13	0.25
Arsenic	-0.18	-0.80
Barium	-0.28	1.10
Beryllium	0.22	0.06
Boron	0.13	-0.12
Cadmium	-0.52	-0.10
Calcium	0	0.29
Chlorine	-0.06	1.75
Chromium	-0.22	-0.29
Cobalt	0.10	0.40
Copper	0.11	-0.88
Fluorine	0	1.41
Iron	-0.23	0.76
Lead	-0.70	-0.56
Magnesium	0.03	1.06
Manganese	-0.12	-1.42
Mercury	0.32	1.40
Molybdenum	0.24	0.67
Nickel	-0.08	0.30
Selenium	-0.13	0
Silver	-0.13	1.28
Sulfur	0.13	--
Titanium	0.21	-0.14
Uranium	0.19	0.12
Vanadium	-0.18	0.20
Zinc	-0.32	-1.22
Average of Normalized Deviations	-0.06	0.26
RMS of Deviations[2]	0.24	0.86

NOTES:

1. Normalized Deviation $= \dfrac{\Sigma_{in}(j) - \Sigma_{out}(j)}{\left(\dfrac{\Sigma_{in}(j) + \Sigma_{out}(j)}{2}\right)}$

2. Root Mean Square of Normalized Deviations $= \sqrt{\dfrac{\displaystyle\sum_j \left[\dfrac{\Sigma_{in}(j) - \Sigma_{out}(j)}{\left(\dfrac{\Sigma_{in}(j) + \Sigma_{out}(j)}{2}\right)}\right]^2}{n}}$

The average total ash distribution for Station I is as follows:

Bottom ash	21.3%
Ash in scrubber slurry	78.4%
Economizer ash	0.05%
Flue gas	0.3%

The distribution of each element in these ashes is given in Table 5-2. A fraction of an element which exceeds the above values in an ash stream indicates enrichment of this element. An element concentration smaller than the above values indicates a depletion of this element in the corresponding ash stream. Corrections for leaching effects of the ashes in contact with water during the sluicing operation were applied by subtracting the element flows in the sluice water inlet from the element flows in the sluice water outlet. An increase in the sluice water outlet concentrations was assumed to arise from leaching effects. The amount leached was added for comparison purposes to the corresponding ash stream. This was possible for all elements with the exception of chlorine and sulfur. The mass flows of these elements in the inlet and outlet liquid streams are high in comparison to the flow in the solids. As a consequence, the errors in the corrected terms are high compared to the mass flow in the solids. Therefore, uncorrected values were used.

The trace element flows in the scrubber sludge were corrected for the contribution from both the lime addition and the water streams. The values listed in Table 5-2 show, therefore, the distribution of elements entering the boiler with the coal among the ash solids.

TABLE 5-2

DISTRIBUTION OF ELEMENTS AMONG BOTTOM ASH, SCRUBBER SLURRY, ECONOMIZER ASH, AND FLUE GAS AT STATION I

Element	lb/hr in Coal	Bottom Ash % (Average 21.3%)	Scrubber Slurry % (Average 78.4%)	Economizer Ash % (Average .05%)	Flue Gas % (Average .3%)
Aluminum	6510	18.0	81.7	0.04	0.25
Antimony	0.15	9.9	89.4	0.02	0.61
Arsenic	0.23	5.0	87.6	0.03	7.5
Barium	37	15.4	83.6	0.04	<0.84
Beryllium	0.23	15.7	83.8	0.04	0.65
Boron	14	7.9	86.2	0.06	5.9
Cadmium	0.051	8.9	84.0	0.18	7.0
Calcium	4980	15.1	84.0	0.05	0.85
Chlorine	12	8.3	16.7	0.02	75.0
Chromium	5.9	10.7	79.4	0.04	9.9
Cobalt	0.59	15.5	81.7	0.08	2.6
Copper	9.6	12.4	87.0	0.03	0.66
Fluorine	40	0	98.0	0.007	2.0
Iron	1130	20.4	80.0	0.04	0.63
Lead	1.2	3.1	94.9	0.01	1.9
Magnesium	821	17.7	81.1	0.05	1.2
Manganese	48	13.6	85.9	0.04	0.38
Mercury	0.037	0.78	12.5	0.0008	86.8
Molybdenum	1.1	8.4	48.3	0.11	43.2
Nickel	2.5	18.3	77.6	0.04	4.1
Selenium	0.62	0	97.8	0.001	2.2
Silver	0.013	9.5	86.1	0.01	4.7
Sulfur	2038	0	37.8	0	62.2
Titanium	311	20.6	79.0	0.05	0.30
Uranium	0.37	50.1	47.7	0.07	2.0
Vanadium	14	16.3	81.1	0.04	2.5
Zinc	6.8	4.4	93.0	0.02	2.5

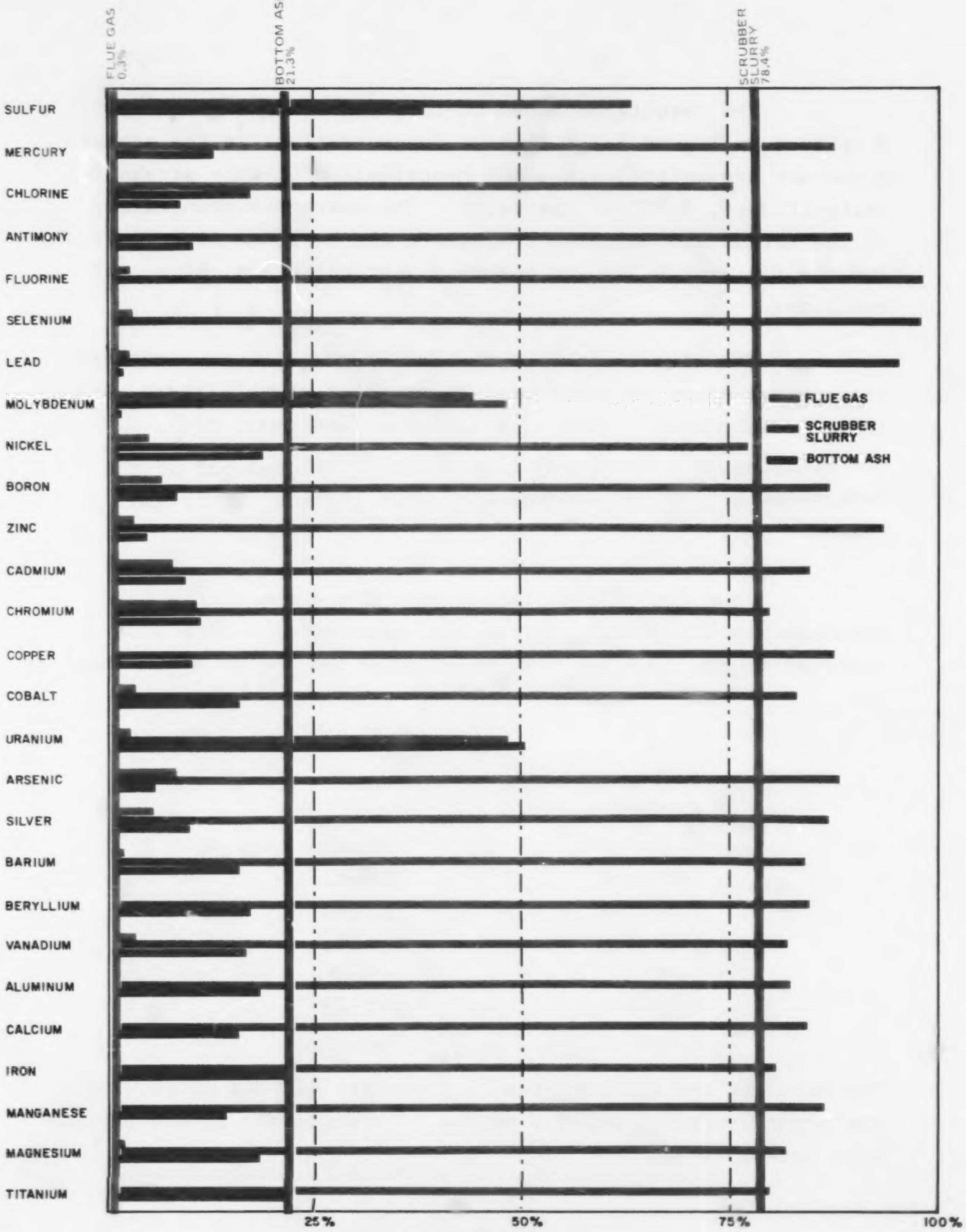

FIGURE 5.1
DISTRIBUTION OF ELEMENTS AMONG BOTTOM ASH,
ASH IN SCRUBBER SLURRY
AND FLUE GAS AT STATION I

The results obtained in this fashion are graphically displayed in Figure 5-1. Element concentrations in the economizer ash are omitted since the contribution of this stream is insignificant, 0.05% of the total. The average concentration of the bottom ash (21.3%), the ash in the scrubber slurry (78.4%) and the fly ash (0.3%) are shown as vertical green, blue, and red lines.

The distribution of the individual elements in these streams are shown as horizontal lines (bottom ash - green, ash in scrubber slurry - blue, fly ash plus flue gas - red). The crossing of a total ash line and an elemental bar of the same color indicates enrichment of that element in the ash stream.

From the exit distributions, the elements can be divided into two groups. Group one comprises the compounds enriched in the flue gas and depleted in the bottom ash. They are:

Sulfur
Mercury
Chlorine
Antimony
Fluorine
Selenium
Lead
Molybdenum
Nickel
Boron
Zinc
Cadmium
Chromium
Copper
Cobalt
Arsenic
Silver
Vanadium

The balances for cadmium, lead and mercury did not close within the error limits, placing a degree of uncertainty in the enrichment data.

Uranium seems to be enriched in the bottom ash. The reasons for this enrichment are not clear. The rest of the elements are evenly distributed among the ashes. This group includes:

Barium
Beryllium
Aluminum
Calcium
Iron
Magnesium
Manganese
Titanium

Probable mechanisms for the element enrichment are:

(1) volatilization of an element or compound in the boiler, or

(2) chemical changes with formation of a volatile element or compound.

The volatilized compounds can subsequently:

(1) leave the plant without recondensation,

(2) recondense partially, or

(3) recondense completely onto the available particulate surface area.

These mechanisms lead to a depletion of the bottom ash and an enrichment in the flue gas and/or precipitator ashes. Element concentration as a function of particle size can elucidate the underlying phenomena. In addition, the types of compounds volatilized would be of extreme practical interest. Both areas were, however, outside the scope of the present study.

APPENDIX A
SAMPLING AT STATION I

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1.0 INTRODUCTION

Sampling at Station I was performed by Radian personnel during the period September 2-5, 1974. Units using different coals and particulate collection devices were selected for sampling under the trace elements' portion of the Northern Great Plains Resources Program. This plant is typical of a plant burning Wyoming coal and equipped with a venturi scrubber for particulate control.

Representative samples of all inlet and outlet streams around the power plant were collected with the objective of quantifying the trace element emissions from the plant. Analyses of the samples for the trace elements of interest in combination with flow rate data for each stream during the sample period allows a material balance to be performed for each element. The material balances serve two main functions: (1) closure of the material balances lends credibility to the sampling and analytical techniques and, therefore, to the emission data produced, and (2) data is generated which allows the ultimate fate of individual trace elements to be determined and their flow through the plant system to be traced.

The following sections provide descriptions of Station I, the sampling techniques used, and the flow rate measurements performed.

2.0 PLANT DESCRIPTION

The unit sampled at Station I consists of a 330 MW, tangentially fired, balanced draft boiler with three venturi scrubbers for fly ash control. A schematic of the plant is shown in Figure 2-1. The boiler is fired with subbituminous coal which is mined about 15 miles from the plant site and transported by rail. The coal for Unit 4 is stored in seven storage silos and gravity fed to seven mills where it is crushed prior to delivery to the boiler through a pneumatic conveyer system.

The three venturi scrubbers use a combination of clear settling pond water and cooling tower blowdown as scrubber liquor with the addition of lime to control the pH to approximately 6.5. The scrubber liquor was recycled to each scrubber at a rate of 6500 gpm during the sampling period. The three scrubbers have a total inlet flue gas capacity of 1.43×10^6 acfm. The flue gas exits the scrubbers through spray demister systems to a stack with a diameter of 32 feet and a decreased diameter orifice at the top to increase exit velocity.

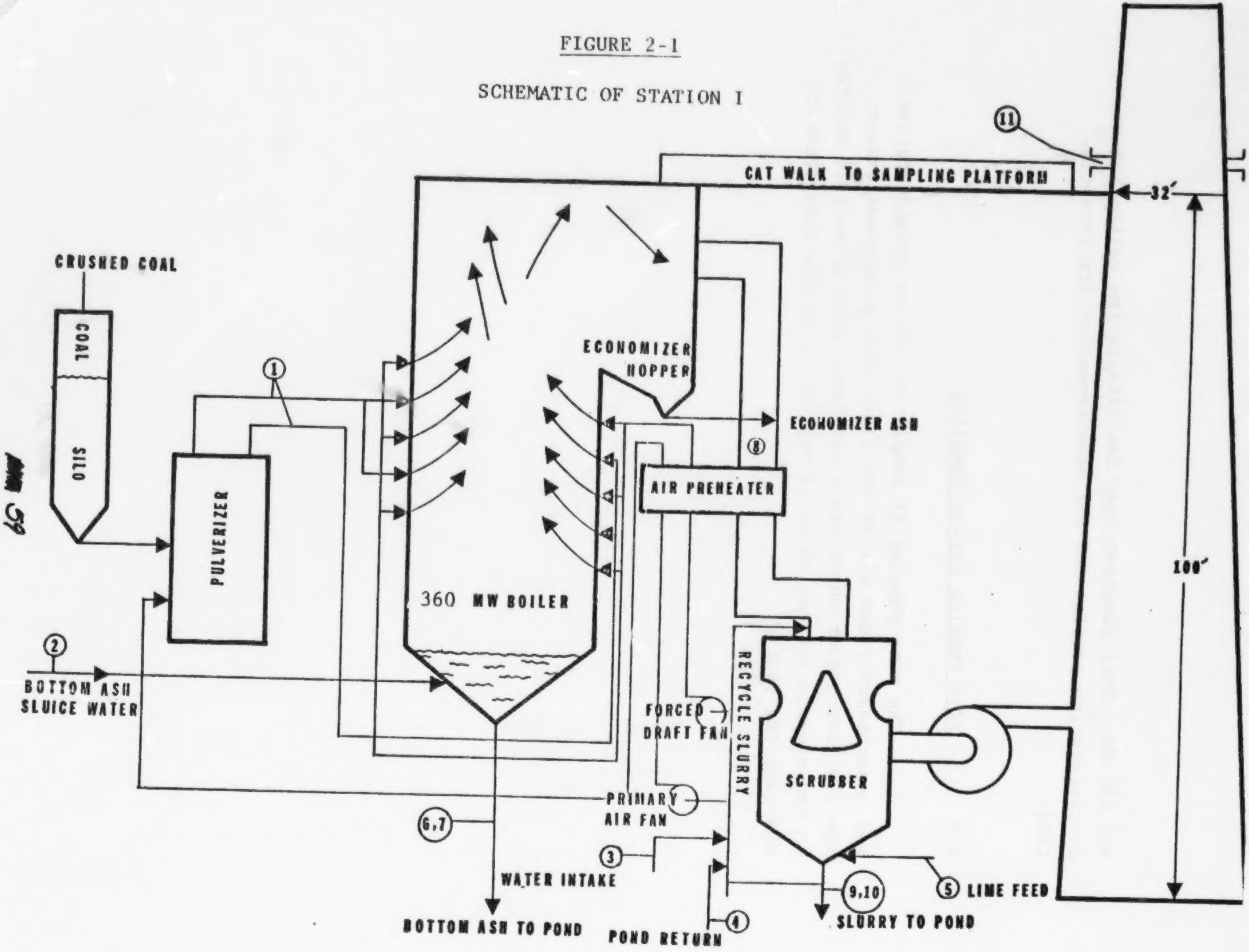
The bottom ash and scrubber sludge from Unit No. 4 are deposited in a settling pond, the clear return from which provides both sluice water and scrubber makeup water. The small quantity of ash collected in the economizer hopper is trucked away periodically.

2.1 Plant Operation During Sampling

Unit No. 4 was operated at an essentially constant load during the sampling period on September 4th varying between 298 MW

FIGURE 2-1

SCHEMATIC OF STATION I


CRUSHED COAL
COAL
SILO
PULVERIZER
①
②
BOTTOM ASH SLUICE WATER
360 MW BOILER
ECONOMIZER HOPPER
ECONOMIZER ASH
⑧
AIR PREHEATER
CAT WALK TO SAMPLING PLATFORM
⑪
32′
100′
FORCED DRAFT FAN
PRIMARY AIR FAN
RECYCLE SLURRY
SCRUBBER
⑥,⑦
③
WATER INTAKE
BOTTOM ASH TO POND
④
POND RETURN
⑨,⑩
SLURRY TO POND
⑤ LIME FEED

and 285 MW. This constant load facilitated the collection of representative samples and the measurement of accurate flow rates.

2.2 Time Phasing During Sampling

The time phasing of sample collection around Station I was unnecessary since all of the flows were continuous except the scrubber liquor which had a residence time of only 20 minutes in the recycle system, which is negligible in the time frame of the sampling period.

3.0 DESCRIPTION OF SAMPLING POINTS

The sample point locations are indicated in Figure 2-1, and the inlet and outlet streams are shown in Figure 3-1. The following sections provide detailed descriptions of the sample points and the techniques used to obtain samples representative of the streams during the sampling period.

3.1 Coal Sampling

Samples of pulverized coal were taken from the pneumatic transfer lines between the mills and the boiler. A cyclone sampler was used to obtain approximately 1.5 lb. of hot, dry coal dust from one of four transfer lines in sequence every 15 to 20 minutes from 8:30 AM to 5:00 PM on September 4, 1974. The individual samples were combined in a large polyethylene container and riffled to yield two one-liter bottles of sample for analysis.

In addition, 3 lb. samples of the coal fed to the storage silos were periodically taken off the conveyer belt from the ready pile. These samples were also combined and riffled to provide two one-liter polyethylene bottles for moisture content determination. This data is necessary for the determination of the dry coal feed rate.

3.2 Bottom Ash Sluice Water Inlet

The sluice water for transporting the bottom ash was pumped from a settling pond located approximately one-half mile

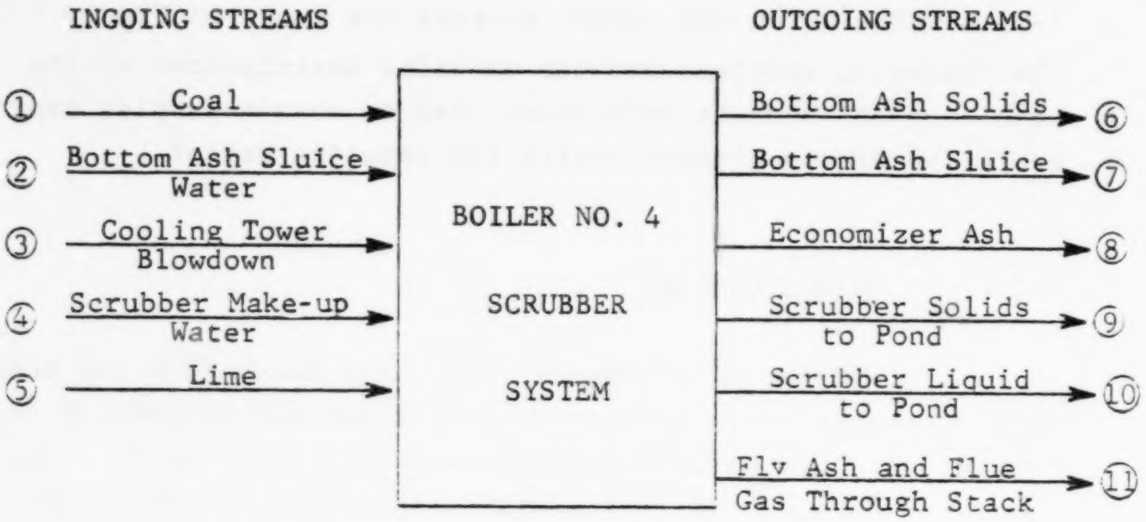

INGOING STREAMS
OUTGOING STREAMS
① Coal
② Bottom Ash Sluice Water
③ Cooling Tower Blowdown
④ Scrubber Make-up Water
⑤ Lime
BOILER NO. 4
SCRUBBER
SYSTEM
Bottom Ash Solids ⑥
Bottom Ash Sluice ⑦
Economizer Ash ⑧
Scrubber Solids to Pond ⑨
Scrubber Liquid to Pond ⑩
Fly Ash and Flue Gas Through Stack ⑪

FIGURE 3-1

In and Outgoing Streams at the
Boiler No. 4 Scrubber System at Station I

from the plant. The particular pond sampled was one of three used for settling of bottom ash and scrubber sludge solids. A two-liter sample was taken from the settling pond in a polyethylene bottle at a point about 15 feet from the intake to the plant. The sample was acidified with nitric acid to preserve it for subsequent analysis.

3.3 Cooling Tower Blowdown

A portion of the cooling tower blowdown is used as pump seal water, demister wash, and induced draft fan spray in the scrubbers. The cooling towers are located next to the settling ponds on the west side of the plant. A two-liter sample was taken at the bottom of the cooling tower, acidified with nitric acid for preservation, and stored in a polyethylene bottle for subsequent analysis.

3.4 Scrubber Makeup Water

The scrubber makeup water comes from the same pond as the bottom ash sluice water and, therefore, the same sample was be used for analysis of both streams. For the sampling procedure and handling of the sample, see Section 3.2.

3.5 Lime

The lime feed to the scrubber slurry makeup tanks was sampled between the lime storage silo and makeup tanks. Samples of approximately 100 g each were taken every hour from 9:20 AM to 4:20 PM on September 4, 1974, with a small scoop. The lime was dry and appeared clean, no discoloration. The individual samples were combined for a composite sample.

3.6 Bottom Ash

Bottom ash from the boiler was continuously sluiced with clear pond water via a 10 in. pipe about one-half mile to the first of two settling ponds. The flow from the pipe was sampled using a 500 ml wide mouth polyethylene bottle. In order to obtain a representative sample, the bottle was passed from bottom to top through the stream three times with the bottle held perpendicular to the direction of flow and the mouth tilted slightly into the flow. Three passes accumulated approximately 350 ml which was emptied into a five gallon polyethylene container. Samples were collected every 15 minutes from 10:00 AM to 5:00 PM on September 4th and combined in the five gallon container. The sample was filtered in the laboratory and the bottom ash solids dried and ground for analysis.

3.7 Bottom Ash Sluice Water Outlet

Two liters of the liquid portion of the bottom ash sluice were removed from the five gallon sample described in Section 3.6, filtered, acidified for preservation, and returned to the laboratory for analysis.

3.8 Scrubber Solids

Scrubber slurry was continuously pumped via an 18 in. diameter pipe about one-half mile to the first of three settling ponds. The stream exiting the pipe was sampled concurrently with bottom ash sampling with a one-liter polyethylene bottle in a manner similar to that described for bottom ash in Section 3.6. Samples were collected every 30 minutes from 10:00 AM to 5:00 PM on September 4th. The longer sampling interval was possible because the density of the scrubber slurry was much more constant than that of the bottom ash sluice. The solids were separated by filtration in the laboratory and dried and ground for analysis.

3.9 Scrubber Liquids

Following the scrubber slurry sample collection described in Section 3.8, the five gallon sample was allowed to stand until most of the solids had settled. A two-liter sample of the supernatant liquor was removed, filtered to remove any fine solids, acidified with nitric acid for preservation, and stored in polyethylene bottles for subsequent analysis.

3.10 Economizer Ash

The ash accumulation in the economizers is periodically emptied into an ash storage silo from which the ash is trucked away. At the beginning of the sampling period the economizer and the storage silo were emptied. At the end of the period the accumulation in the economizer was emptied into the silo and the silo emptied into two large polyethylene containers. The ash was randomly cored and the sample riffled to provide a two-liter sample for analysis

3.11 Fly Ash

Particulate matter in the exiting flue gas was sampled through four ports located at the ends of two perpendicular diameters of the stack serving Unit No. 4. These ports were approximately 100 feet above ground level; the stack internal diameter was 32 feet at this point: The flue gas was relatively cool, 114°F, following passage through the venturi scrubbers and had a large amount of entrained water from the spray demister system. The moisture content was found to be 16.0% by condensation measurements. This is above the saturation level of 11.7% at the gas temperature indicating a significant quantity of entrained mist.

Since the sample ports were only 2½ stack diameters downstream from the point of entry of the flue gas, a total of 40 traverse points were necessary to statistically sample the stream. The stack cross-section was divided into ten concentric sections of equal area and the samples were taken at the centroid of each section along the two perpendicular diameters as per EPA Method 1. The sampling points were the following distance from the inner wall of the stack at each of the four ports:

1. 5 in.
2. 1 ft. 3 in.
3. 2 ft. 2 in.
4. 3 ft. 1 in.
5. 4 ft. 2 in.
6. 5 ft. 3 in.
7. 6 ft. 6 in.
8. 8 ft. 0 in.
9. 9 ft. 10 in.
10. 12 ft. 5 in.

Velocity traverses of the stack were made on September 2nd and in conjunction with the particulate loading determinations on September 3rd and 4th as per EPA Method 2. The average velocity was found to be 25.9 fps over the three-day period with less than ten percent variation over the time period or from point-to-point in the traverses. The velocity traverses determined the total flow in the stack and the conditions necessary for isokinetic sampling.

Particulate loading determinations were made on September 3rd and 4th with "in stack" Gelman filter devices at the end of a heat traced sample probe. These determinations were a combination of dynamic grain loadings, for which the loadings at the points from each port were physically averaged by sampling for an equal time interval at each point with the accumulation of all ten points on a single filter, and single point grain loadings at point 8 to define the actual particulate concentration at the point used for particulate sample collection. During particulate loading determinations, the moisture content of the flue gas was measured by condensation in an efficient copper tubing condenser maintained in an ice bath.

Particulate matter in the stack gas stream was sampled at point 8 from the south and east ports on September 4th during the period when the other plant streams were sampled. The wet electrostatic precipitator (WEP) sampling system used for sample collection is shown schematically in Figure 3-2. A five percent sulfuric acid solution is circulated in this sampling device by a peristaltic pump. A voltage of 12-14 KV is applied between a thin platinum wire and the wetted wall to induce electrostatic collection. The sampling probe from the sampling nozzle to the WEP was lined with teflon tubing to prevent trace element contamination of the sample. A gas stream is isokinetically drawn from the stack and through the sampling equipment by a vacuum pump and metered by a dry gas meter. Approximately three hours of sampling was required to obtain sufficient particulate matter for analysis.

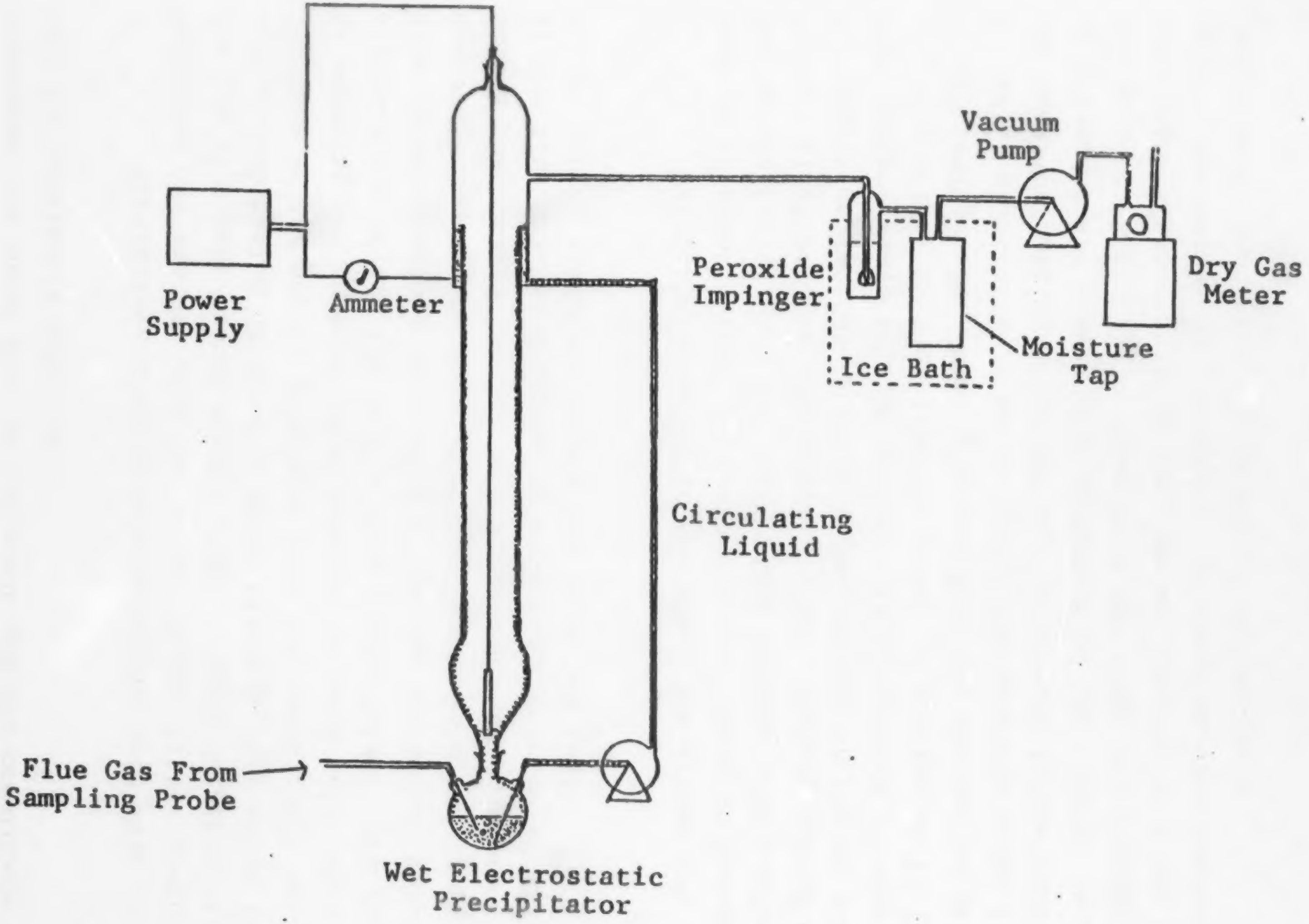

Power Supply
Ammeter
Vacuum Pump
Peroxide Impinger
Dry Gas Meter
Ice Bath
Moisture Tap
Circulating Liquid
Flue Gas From Sampling Probe
Wet Electrostatic Precipitator

FIGURE 3-2

SCHEMATIC OF STATION I
ARRANGEMENG FOR DUCT SAMPLING

Samples for mercury were taken in the middle and at the end of the last WEP run by diverting the exit gas flow from the WEP through a mesh of gold wire where the mercury is collected by amalgamation with the gold. Samples were also taken during the WEP runs for the determination of the sulfur concentration in the flue gas by bubbling a known volume of gas through a hydrogen peroxide solution as per EPA Method 6. Orsat analysis of the flue gas for oxygen and carbon dioxide was performed to provide gas density information as per EPA Method 3.

3.12 Sampling Schedule

The samples described in the preceding sections were taken during the period September 2, 3, and 4, 1974, according to the schedule shown in Figure 3-3. Those samples enclosed in parenthesis are to be analyzed, the rest being held in reserve.

		Sept. 2	Sept. 3	Sept. 4
1.	Coal		—	(—)
2.	Bottom Ash Sluice Water Inlet		•	(•)
3.	Cooling Tower Blowdown		•	(• •)
4.	Scrubber Makeup Water		•	(•)
5.	Lime		•	(•••••••)
6.	Bottom Ash		—	(—)
7.	Bottom Ash Sluice Water Outlet		—	(—)
8.	Scrubber Solids		—	(—)
9.	Scrubber Liquid		—	(—)
10.	Economizer Ash			(—•)
11.	Flue Gas Velocity	—	—	—
12.	Flue Gas Particulate Loading		—	—
13.	Flue Gas WEP Particulate Collection		=	(=)

FIGURE 3-3

Sampling Schedule at Station I

4.0 FLOW RATE MEASUREMENTS

The mass flow rate of each of the sampled streams described in Sections 3.0 to 3.11 was determined as described in the following sections.

4.1 Coal

The feed rate of coal to each of seven mills is recorded in the master printout in the control room. The totals for each mill on an hourly basis are provided. The hourly total coal feed rate to the boiler is calculated by averaging the seven mills during the sampling period. Samples were collected of the coal feed to the silos and moisture content determined to allow the coal feed rate to the boiler to be corrected to dry weight basis. The feed rate determined by this method was 2.83×10^5 lb/hr.

This rate was checked by calculating the fuel requirements of the boiler from the hourly plant load in the control room printout, unit heat rate, and the heating value of the coal. This method gives a coal feed rate of 2.84×10^5 lb/hr.

4.2 Bottom Ash Sluice Water Inlet

The bottom ash sluice water was pumped from the settling pond by a centrifugal pump with a 19-3/8 in. impeller driven by a three phase 4160 volt motor. The electrical power requirements of the pump motor were measured by a wattmeter and an ammeter both of which were read hourly during the sampling period on September 4th. The motor power requirement was read directly from the wattmeter in kilowatts and calculated from the ammeter readings. The averages of these two determinations were converted to the pump horsepower requirement using a 93% motor efficiency. The pump curves provided by the manufacturer were used to convert horsepower to a flow of 1.55 x 10^5 gal/hr (2580 gpm) or 1.29 x 10^6 lb/hr.

4.3 Cooling Tower Blowdown

A portion of the cooling tower blowdown is transported to the scrubbers by two pumps. The pressure on the suction and discharge side of each pump was recorded hourly from 9:00 AM to 5:00 PM on September 4th. The total dynamic head developed across the pumps was then used to determine from pump curves supplied by the manufacturer a total flow of 5.27 x 10^4 gal/hr (879 gpm) or 4.39 x 10^5 lb/hr.

4.4 Scrubber Makeup Water

The scrubber makeup water was measured by a flowmeter on the inlet line to each of the three scrubbers. Readings were taken from these meters hourly from 9:00 AM to 5:00 PM on September 4th. The total flow rate to the three was averaged over the entire period and found to be 4.80 x 10^5 gal/hr (8002 gpm) or 4.00 x 10^6 lb/hr.

4.5 Lime

The lime feed to the scrubber slurry makeup tank was calculated from a material balance for calcium around the boiler-scrubber system. The calcium material balance is expressed as:

$$
\begin{aligned}
& M_c XW_c(Ca) + M_{swi} XW_{swi}(Ca) + M_{ctb} XW_{ctb}(Ca) \\
& + M_{mw} XW_{mw}(Ca) + M_l XW_l(Ca) = M_{ba} XW_{ba}(Ca) \\
& + M_{swo} XW_{swo}(Ca) + M_{ss} XW_{ss}(Ca) + M_{sl} XW_{sl}(Ca) \\
& + M_{ea} XW_{ea}(Ca) + V_{fg} XV_{fg}(Ca)
\end{aligned}
$$

where,

M_c = the mass flow rate of coal into the boiler on a dry weight basis (lb/hr)

$XW_c(Ca)$ = the weight fraction of calcium in the coal on a dry weight basis

M_{swi} = the mass flow rate of bottom ash sluice water into the ash sluice system (lb/hr)

$XW_{swi}(Ca)$ = the weight fraction of calcium in the inlet bottom ash sluice water which is the same as clear pond return

M_{ctb} = the mass flow rate of cooling tower blowdown to the scrubber system (lb/hr)

$XW_{ctb}(Ca)$ = the weight fraction of calcium in the cooling tower blowdown

M_{mw} = the mass flow rate of the make-up water from the settling pond to the scrubber system

$XW_{mw}(Ca)$ = the weight fraction of calcium in the make-up water to the scrubber system which is the same as clear pond return

M_l = the mass flow rate of lime into the scrubber system (lb/hr)

$XW_l(Ca)$ = the weight fraction of calcium in the lime

M_{ba} = the discharge rate of bottom ash from the boiler (lb/hr)

$XW_{ba}(Ca)$ = the weight fraction of calcium in the bottom ash

M_{swo} = the mass flow rate of the bottom ash sluice water from the sluice system which is equal to M_{swi} (lb/hr)

$XW_{swo}(Ca)$ = the weight fraction of calcium in the scrubber discharge solids

M_{sl} = the discharge rate of liquid from the scrubber system (lb/hr)

$XW_{sl}(Ca)$ = the weight fraction of calcium in the scrubber discharge liquid

M_{ea} = the discharge rate of economizer ash (lb/hr)

$XW_{ea}(Ca)$ = the weight fraction of calcium in the economizer ash

V_{fg} = the volumetric flow rate of the flue gas in the stack (scfh)

$XV_{fg}(j)$ = the weight of calcium per unit volume of flue gas (lb/scf)

The lime flow rate is calculated by solving this equation for M_1. The concentrations of calcium, flowrates, and resulting mass flows of calcium used to calculate M_1 are presented in Table 4-1. This gives a lime flowrate of 4.78×10^3 lb/hr.

4.6 Bottom Ash

Determination of the bottom ash production rate directly was impossible because no sample of the bottom ash sluice stream could be obtained which accurately represented the percent solids in the stream. Random fluctuations in the solids content of the sluice stream were evident throughout the sampling period. The bottom ash production rate was, therefore, determined indirectly from the ash content of the coal, the coal feed rate (Section 4.1), the economizer ash flow rate (Section 4.10), the scrubber solids flow rate (Section 4.8), and the ash content of the scrubber solids. The ash content of the scrubber solids was determined by analysis of the economizer ash, the scrubber solids, and the lime feed for titanium. Assuming that the concentration of Ti in the ash in the scrubber solids is equal to the Ti concentration in the economizer ash, the ash content of the scrubber solids was calculated. The accuracy of this technique was greatly enhanced by the high Ti concentration in the ash compared to the lime Ti concentration. From an ash content of the dry scrubber solids of 84.9% and ash content of the coal of 19.12% (dry basis), the production rate of bottom ash was found to be 1.15×10^4 lb/hr.

TABLE 4-1

SUMMARY OF CALCIUM MATERIAL BALANCE DATA

Stream	Calcium Concentration	Flow Rate	Calcium Flow Rate
Coal	1.76%	2.83×10^5 lb/hr	4.98×10^3 lb/hr
Bottom Ash Sluice Water Inlet	790 ppm	1.29×10^6 lb/hr	1.02×10^3 lb/hr
Cooling Tower Blowdown	140 ppm	4.39×10^5 lb/hr	61.5 lb/hr
Scrubber Make-up Water	790 ppm	4.00×10^6 lb/hr	3.16×10^3 lb/hr
Lime	53.5%	M_1	$.535\ M_1$
Bottom Ash	8.66%	1.15×10^4 lb/hr	9.96×10^2 lb/hr
Bottom Ash Sluice Water Outlet	790 ppm	1.29×10^6 lb/hr	1.02×10^3 lb/hr
Scrubber Solids	11.8%	5.00×10^4 lb/hr	5.9×10^3 lb/hr
Scrubber Liquid	910 ppm	4.18×10^6 lb/hr	3.80×10^3 lb/hr
Economizer Ash	11.5%	26.3 lb/hr	3 lb/hr
Flue Gas	1.12×10^{-6} lb/scf	5.01×10^7 scfh	56 lb/hr

4.7 Bottom Ash Sluice Water Outlet

The bottom ash sluice water outlet flow rate is equal to the inlet flow rate determined as described in Section 4.2 to be 1.55×10^5 gal/hr (2580 gpm) or 1.29×10^6 lb/hr.

4.8 Scrubber Solids

The flow rate of scrubber solids from the three venturi scrubbers to the settling pond was determined from the weight percent solids in the scrubber sludge stream to the pond and the volumetric flow of liquid from the scrubber. The volumetric flow of liquid from the scrubber was determined by a water material balance which will be described in Section 4.9. With a slurry stream solids concentration of 1.18%, the mass flow of solids from the scrubbers was found to be 5.00×10^4 lb/hr.

4.9 Scrubber Liquid

As mentioned in Section 4.8, the liquid flow from the scrubber was determined from a water material balance around the scrubber system. The inlet water streams to the system consist of the scrubber makeup water (see Section 4.4), the cooling tower blowdown added to the scrubber system (see Section 4.3), and the water originating in the boiler from the combustion reactions and the moisture content of the coal. The outlet water flow from the scrubber system is the sum of the liquid portion of the sludge stream to the pond and the evaporation and entrainment losses to the exiting flue gas. The water leaving the system in the flue gas was determined by condensation during stack sampling (Section 3.11). Since all of the flow rates are known or calculable except the scrubber liquid flow, this flow can be determined. This water balance indicates a scrubber liquid flow to the settling pond of 4.18×10^6 lb/hr.

4.10 Economizer Ash

The amount of economizer ash produced during the eight hour sampling period on September 4th was measured by emptying the economizers and economizer ash silo at the beginning of the test period and measuring the accumulation over the period. The ash was collected in two large polyethylene containers and its volume determined to be 2.70 cu. ft. From this volume and a packed density of 1.25 g/ml (78.0 lb/cu. ft.), the production rate of economizer ash during the sampling period was calculated to be 26.3 lb/hr.

4.11 Fly Ash

The flow rate of fly ash from the Unit No. 4 stack at Station I was determined from the flue gas velocity and particulate loading measurements discussed in Section 3.11. The total quantity of flue gas, corrected to standard conditions, passing through the stack is calculated from the average gas velocity in the stack and the cross-sectional area of the stack at the point of measurement. From the average velocity given in Section 3.11 of 25.9 fps and a cross-sectional area of 804 square feet, the total flow from the stack on a dry basis was 8.35×10^5 scfm. The fly ash emissions were then found from the total flow and an average particulate loading of 0.023 gr/scf to be 164 lb/hr.

4.12 Summary of Flow Rates

The mass flow of each of the streams sampled at Station I are summarized in Table 4-2. The flow rates of all solids are based on a dry weight basis.

TABLE 4-2

FLOW RATES FOR STREAMS AROUND STATION I

Stream	Flow Rate
Coal	2.83×10^5 lb/hr.
Bottom Ash Sluice Water Inlet	1.29×10^6 lb/hr.
Cooling Tower Blowdown	4.39×10^5 lb/hr.
Scrubber Makeup Water	4.00×10^5 lb/hr.
Lime	4.78×10^3 lb/hr.
Bottom Ash	1.15×10^4 lb/hr.
Bottom Ash Sluice Water Outlet	1.29×10^6 lb/hr.
Scrubber Solids	5.00×10^4 lb/hr.
Scrubber Liquid	4.18×10^5 lb/hr.
Economizer Ash	26.3 lb/hr.
Flue Gas	5.01×10^7 scfh
Fly Ash	164 lb/hr.

APPENDIX B
ANALYTICAL PROCEDURES

APPENDIX B

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BIBLIOGRAPHY

Trace element analyses on samples from three power plants were performed using dissolution and analytical techniques adapted specifically for these matrices.

1.0 SAMPLE PREPARATION

Preparation procedures were performed on the following types of samples to provide the primary digestion solution:

Coal
Coal Ash
Sludge
Lime
Wet electrostatic precipitator
Aqueous streams and filtrates

1.1 Coal, Coal Ash, and Sludge Preparation

The dissolution of coal, coal ash, and sludge is achieved by a two-step method. The samples are oxidized at 850-950°C in the presence of air utilizing a quartz pipe reactor. Volatile trace elements are retained via an acetone-dry ice trap at the end of the reactor. Dissolution of the remaining solids is accomplished by treatment with hydrofluoric, nitric, and sulfuric acid. The dissolved solids are then combined with the washings from the cold trap.

1.2 Lime/Limestone Preparation

Lime is dissolved by treatment with 5% hydrochloric acid. Any remaining undissolved material is removed by filtration and treated with hydrofluoric, nitric, and sulfuric acids to achieve dissolution.

1.3 WEP Preparation

An .8μ millipore filter was used to remove particulates from aqueous WEP samples. The particulates were then treated similar to coal (through the quartz pipe reactor acid dissolution steps). The filtrates, dissolved solids, and cold trap washings were quantitatively transferred to a single container to form the primary digestion sample.

1.4 Aqueous Streams and Filtrates Preparation

Nitric acid was added as a preservative to all aqueous samples.

2.0 ANALYTICAL PROCEDURES

The following analytical procedures were utilized for the determination of trace elements in the various samples. Each analytical technique has been screened for accuracy and reliability by standard addition and interference studies.

The complete analytical scheme for the analysis of trace elements in the samples are found in Figures 2-1, 2-2, 2-3, and 2-4. Detection limits for each procedure are summarized in Table 2-1.

2.1 Determination of Fluoride by the Ion-Selective Electrode Technique

The determination of fluoride utilizes a sodium carbonate fusion for solid samples (TH-060) and direct analysis of aqueous samples. The technique of standard addition using a fluoride specific-ion electrode, mentioned by several workers (BA-131, BA-137), is used for measurement of the fluoride ion. A citrate buffer is used to release complexed fluoride ions and to stabilize the pH and ionic strength. Addition of a standard quantity of fluoride is characterized by a change in the potential of the solution. The specific ion electrode senses this change in potential which is related to the initial fluoride concentration. The relationship between potential and fluoride concentration follows the Nernst equation:

$$\Delta E = A \log (C_F + X_1)/C_F$$

where,

ΔE is the change in potential

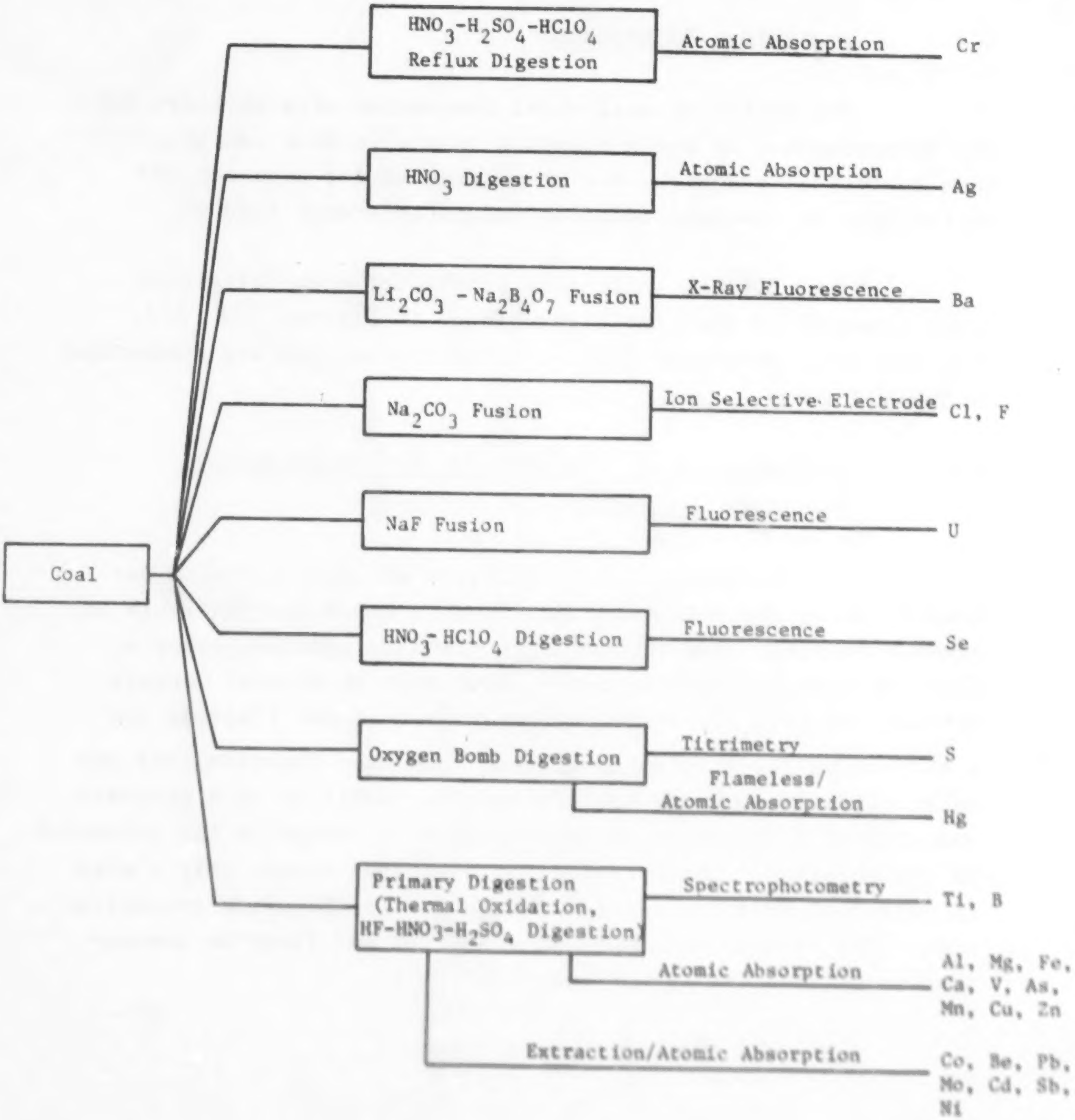
Coal
HNO_3-H_2SO_4-$HClO_4$ Reflux Digestion
Atomic Absorption
Cr
HNO_3 Digestion
Atomic Absorption
Ag
Li_2CO_3 - $Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
Na_2CO_3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO_3-$HClO_4$ Digestion
Fluorescence
Se
Oxygen Bomb Digestion
Titrimetry
S
Flameless/ Atomic Absorption
Hg
Primary Digestion (Thermal Oxidation, HF-HNO_3-H_2SO_4 Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni

FIGURE 2-1

ANALYSIS PROCEDURE FOR TRACE ELEMENT ANALYSIS OF COAL

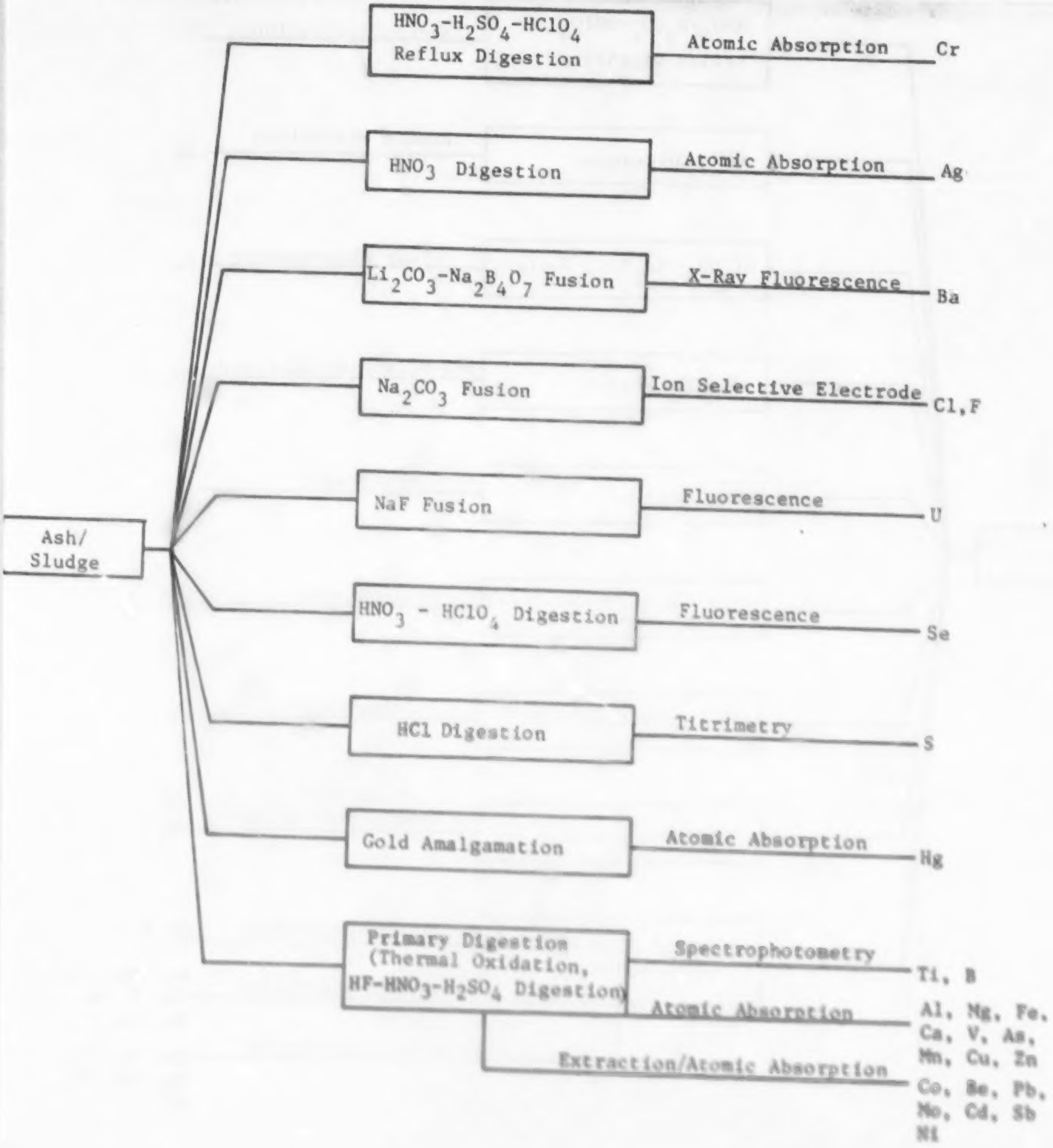
Ash/
Sludge
HNO3-H2SO4-HClO4
Reflux Digestion
Atomic Absorption
Cr
HNO3 Digestion
Atomic Absorption
Ag
Li2CO3-Na2B4O7 Fusion
X-Ray Fluorescence
Ba
Na2CO3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO3 - HClO4 Digestion
Fluorescence
Se
HCl Digestion
Titrimetry
S
Gold Amalgamation
Atomic Absorption
Hg
Primary Digestion
(Thermal Oxidation,
HF-HNO3-H2SO4 Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe,
Ca, V, As,
Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb,
Mo, Cd, Sb
Ni

FIGURE 2-2

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS
OF COAL ASH AND SLUDGE

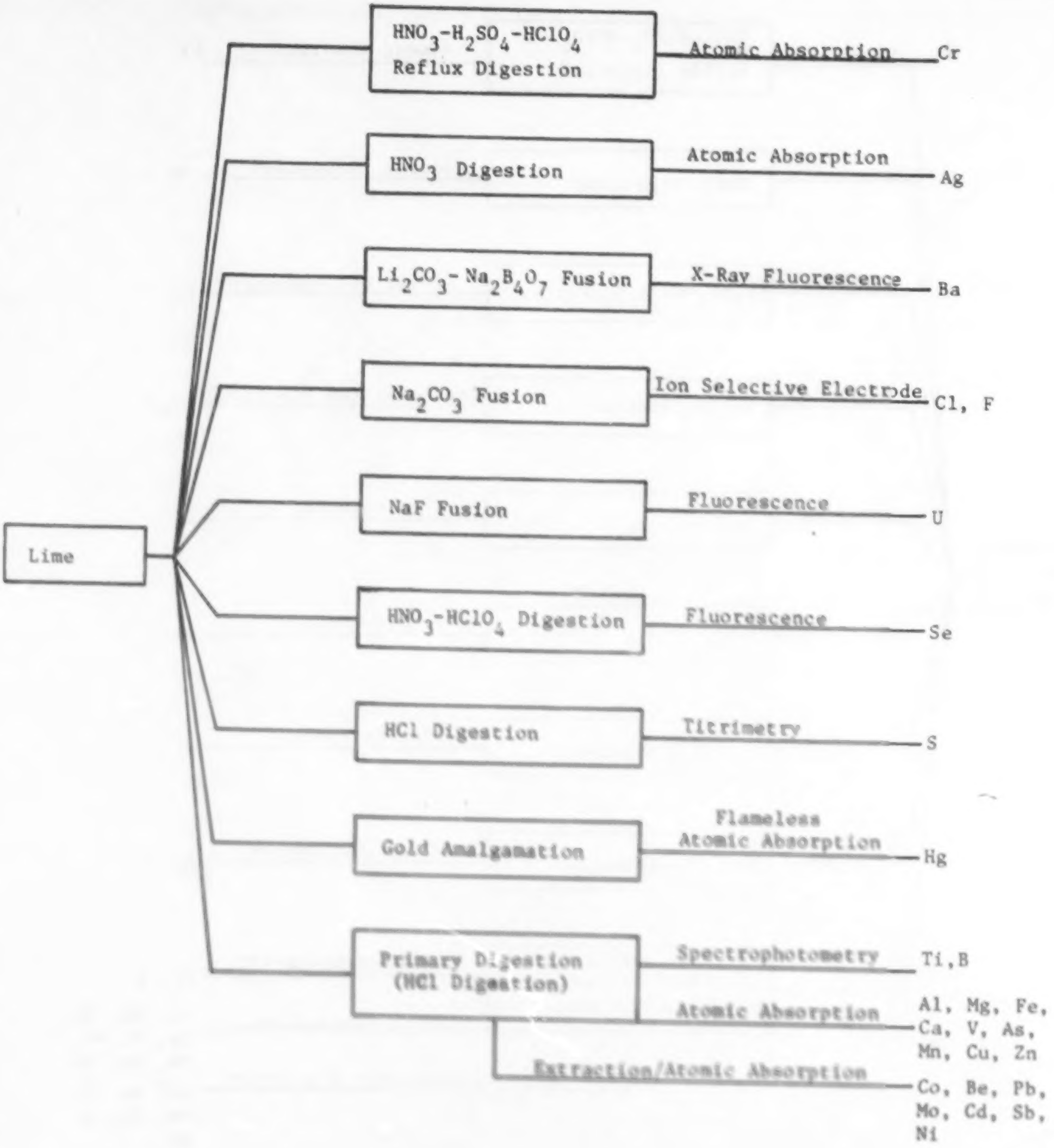
Lime
HNO_3-H_2SO_4-$HClO_4$ Reflux Digestion
Atomic Absorption
Cr
HNO_3 Digestion
Atomic Absorption
Ag
Li_2CO_3-$Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
Na_2CO_3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO_3-$HClO_4$ Digestion
Fluorescence
Se
HCl Digestion
Titrimetry
S
Gold Amalgamation
Flameless Atomic Absorption
Hg
Primary Digestion (HCl Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni

FIGURE 2-3

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS OF LIME

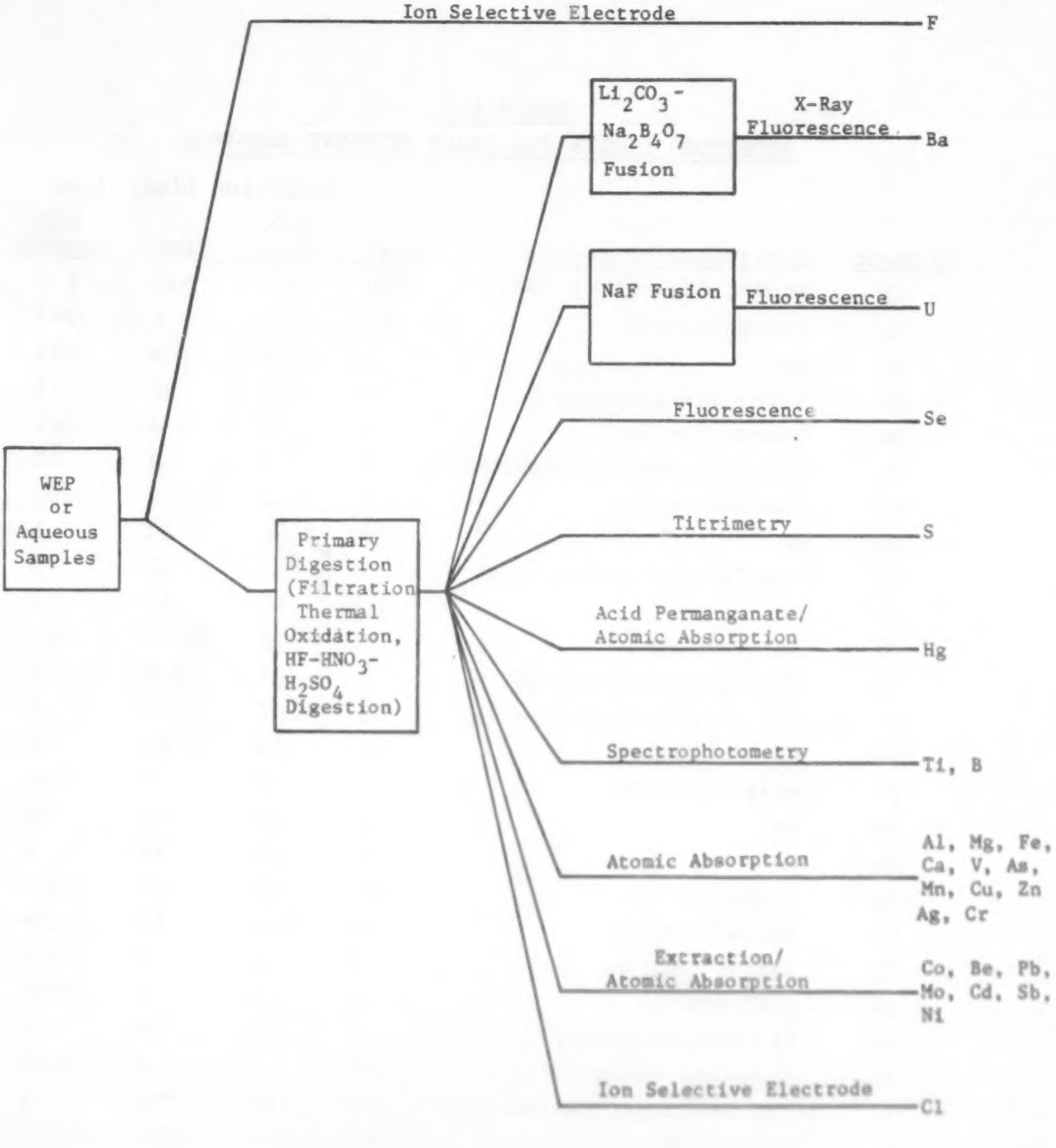
Ion Selective Electrode
F
Li2CO3-Na2B4O7 Fusion
X-Ray Fluorescence
Ba
NaF Fusion
Fluorescence
U
Fluorescence
Se
WEP or Aqueous Samples
Titrimetry
S
Primary Digestion (Filtration Thermal Oxidation, HF-HNO3-H2SO4 Digestion)
Acid Permanganate/ Atomic Absorption
Hg
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn Ag, Cr
Extraction/ Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni
Ion Selective Electrode
Cl

FIGURE 2-4

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS OF WET ELECTROSTATIC PRECIPITATOR LIQUORS AND AQUEOUS SAMPLES

TABLE 2-1

DETECTION LIMITS FOR TRACE ELEMENT ANALYSIS

Element	Analytical Procedure	Detection Limit (ppm) Coal	Ash Sludge	Lime	WEP Aqueous
Al	Atomic Adsorption (AA)	100	400	650	1.0
Sb	Extraction/AA	.04	.16	.6	.002
As	AA	.1	.5	.06	.001
Ba	X-Ray Fluorescence	5	50	40	.5
Be	Extraction/AA	.2	1.6	1.0	.001
B	Ion Exchange/Spectrophotometry	1	3	3	.05
Cd	Extraction/AA	.1	.2	.2	.0002
Ca	AA	10	40	65	.1
Cl	Ion Selective Electrode	5	10	10	.5
Cr	AA	10	40	65	.1
Co	Extraction/AA	.2	.8	1	.003
Cu	Standard Addition/AA	1	4	6.5	.1
F	Ion Selective Electrode	.5	1.2	1.2	.1
Fe	AA	10	40	65	.1
Pb	Extraction/AA	.4	.8	5	.004
Mn	AA	10	40	65	.01
Mg	AA	5	20	30	.5
Hg	Flameless AA	.01	.01	.01	.0005
Mo	Extraction/AA	.4	1.6	16	.004
Ni	Extraction/AA	2	8	2	.006
Se	Fluorometry	.1	.1	.1	.0005
Ti	Spectrophotometry	5	20	20	.1
Ag	Standard Addition/AA	.05	.2	.3	.0005
S	Ion Exchange/Titrimetry	100	100	200	5
U	Fluorometry	.0001	.0001	.0001	.0001
V	Standard Addition/AA	1	4	6.5	.005
Zu	Standard Addition/AA	1	4	6.5	.01

A is the constant = 59 mV at 25°C

C_F is concentration of free fluoride in solution

X_i is additional fluoride concentration added.

2.2 Determination of Chloride by Ion-Selective Electrode

Chloride is determined by a known standard addition method (OR-016). Sample preparation is the same as fluoride with a sodium carbonate fusion for all solid samples and direct analysis of aqueous solutions. A known amount of the species being measured is added to a known volume of sample and the resulting change in potential is observed. The original sample concentration is computed using a known addition table. The method allows samples to be analyzed which have variable ionic strength.

2.3 Spectrophotometric Determination of Titanium

Titanium is determined in the primary digestion solution as a yellow complex formed with tiron (disodium -1, 2- dihydroxybenzene -3, 5- disulfonate). This method is based on the procedure of Yoe and Armstrong, and is further extended to include shales by Rader (RA-125). An acetate buffer is used to regulate the pH. The only major interference is the complex tiron forms with Fe. This interference is eliminated by addition of sodium dithionite, reducing ferric to ferrous ion. The absorbance of the complex is read on a double beam spectrophotometer and samples compared with a standard calibration curve.

2.4 Determination of Copper and Zinc by Atomic Absorption

Copper and zinc are determined by direct aspiration of the primary digestion into the flame of the atomic absorption spectrophotometer (PE-115). Quantitative determinations are achieved by comparing the samples to their respective standards and by the use of standard additions to the primary digestions.

2.5 Determination of Molybdenum by Atomic Absorption

Molybdenum analysis is based on organic extraction atomic absorption technique and method of Joyner (JO-012) which has been modified by Kinrade and Van Loon (KI-085). Molybdenum in the primary digestion readily forms a complex with ammonium pyrrolidinedithiocarbamate at an acidic pH. Extraction of this complex with methyl isobutyl ketone offers a convenient method of concentration of the element. The signal is further enhanced by use of a nitrous oxide-acetylene flame. Concentration was determined by use of a standard calibration curve.

2.6 Determination of Nickel and Cobalt

Nickel and cobalt analyses are based on the organic extraction atomic absorption technique and method of Joyner (JO-012). An ammonium tartrate buffer is used to stabilize the primary digestions. Nickel and cobalt are complexed with the chelating agent sodium diethyldithiocarbamate and extracted with methyl isobutyl ketone.

Once the metal complex has been separated and concentrated in the organic phase, the solution can be directly aspirated into atomic absorption spectrophotometer for measurement of the metal concentration.

2.7 Determination of Arsenic by Flameless Atomic Absorption

Arsenic is determined by a Radian modified flameless atomic absorption procedure based on the method of Ramakrishna, Robinson and West (RA-147) incorporation the techniques of Ediger (ED-027). The usually volatile arsenic present in the primary digestion is complexed as the molybdenum heteropoly acid with ammonium molybdate in a nitric acid medium. The complex formation enables the complex to be analyzed on the graphite furnace by reducing the volatility of the arsenic so that high temperature charring can be used to rid the sample of matrix interferences.

2.8 Determination of Antimony by Flameless Atomic Absorption

Antimony determination is based on a Radian flameless atomic absorption method modifying the extraction procedure of Burke (BU-136) and Headridge and Smith (HE-094) while utilizing the techniques of Ediger (ED-027) to reduce the volatility of antimony. After complexation with iodide, antimony is extracted from the primary digestion into a methyl isobutyl ketone and tributyl phosphate mixture (MIBK-TBP). TBP increases the extraction efficiency. As with arsenic, ammonium molybdate is used to increase the thermal stability of the complex during the charring cycle in the graphite furnace.

2.9 Determination of Beryllium by Atomic Absorption

The method of Bokowski (BO-027) is used for the determination of beryllium by atomic absorption. After addition of EDTA to the primary digestion to mask interferences, the beryllium present in the aqueous sample is chelated with acetylacetone. The complex is then extracted with methyl isobutyl ketone and the organic phase directly aspirated into the atomic

absorption spectrophotometer for the determination of beryllium. The solvent extraction procedure allows one to conveniently separate and concentrate the beryllium present.

2.10 Fluorometric Determination of Uranium

Radian's uranium procedure is a modification of the fluorometric determination of Thatcher (TH-049) updated by Turner (TU-025). Hexavalent uranium ions have a native fluorescence that may be used for analysis in relatively high concentrations. However, when fused with fluoride salts, uranyl ions produce an intense specific fluorescence detectable at levels of 10^{-10} grams of uranium. In general, the solid sample is mixed with a sodium fluoride flux and fused to a translucent disc in a platinum crucible. Aqueous primary digestions are evaporated in platinum crucibles and the residue fused with the flux. Once cooled, its fluorescence is measured with a Turner filter fluorometer. The method of standard additions is used to compensate for quenching.

2.11 Determination of Lead and Cadmium by Atomic Absorption

The procedure for analysis of lead and cadmium is similar to that for copper and zinc found in Section 2.4. Trace elements present in the primary digestion are separated and concentrated by chelation and extraction. Kinrade and Van Loon's method (KI-085) utilizing two chelating agents, ammonium pyrrolidinedithiocarbamate (APDC) and diethyl ammonium diethyldithiocarbamate (DDDC) to complex lead and cadmium has been highly successful. A citrate buffer was used due to its stability, strong buffering capacity, and nonparticipation in any reaction. The sample solution was extracted into methyl isobutyl ketone

and the organic solution injected into the graphite furnace on the atomic absorption spectrophotometer. Concentration was determined by use of a standard calibration curve.

2.12 Fluorometric Determination of Selenium

Selenium in the form of selinite reacts with aromatic orthodiamines to form piazselenols which fluoresce in various organic solvents. This method of determination of selenium is a Radian modification of a procedure published by Levesque and Vendette (LE-068). The solid sample is digested with nitric and perchloric acids in the Parr acid digestion bomb (HA-258). Aqueous samples are heated with nitric and perchloric acids. In both cases this oxidizes selenium to selenate and is followed by hydrochloric acid reduction to selinite. Isolation of selenite from interferring substances is accomplished by adding hydroxylamine, EDTA, and formic acid. The selenite is then reacted with 2, 3-diaminonaphthalene to form the organic extractable piazselenol, naphtho-(2, 3-d)-2 selena-1, 3-diazole, which is determined fluorometrically. This method is free of any interferences and is capable of detecting nanograms of selenium by use of a calibration curve.

2.13 Determination of Vanadium and Silver by Flameless Atomic Absorption

Vanadium is determined by flameless atomic absorption using the heated graphite atomizer. The method is a Radian adaptation of the work of Cioni, Innocente and Mazzioli (CI-002). Standard additions are performed on the primary digestion solution. Experimentation conducted on National Bureau of Standards samples of coal and coal ash yield results within 10% of the certified values.

Huffman (HU-095) recommends the same procedure for silver. Solid samples are dissolved in concentrated nitric acid and the method of standard additions is utilized.

2.14 Determination of Barium by X-ray Fluorescence

Barium is determined by a Radian method utilizing X-ray fluorescence. Samples are pelletized in a solid flux of lithium carbonate-sodium borate which are then introduced directly into the X-ray unit. Quantitative determinations are achieved by comparing the samples to a barium standard calibration curve prepared in the same manner and by the use of the method of standard additions to correct for matrix interferences, if any are present.

2.15 Determination of Chromium, Calcium, Iron, Magnesium, Manganese and Aluminum by Atomic Absorption

Chromium, calcium, iron, magnesium, manganese and aluminum (PE-115) are determined by direct aspiration into the flame of the atomic absorption spectrophotometer. Calcium and magnesium are diluted with lanthanum chloride to mase interferences. All elements are compared with standard calibration curves. All analyses are performed on the primary digestion solutions except chromium.

Chromium requires a special preparation for solid samples. Digestion of coal, ash, limestone, and sludge is accomplished with nitric, sulfuric, and perchloric acids in a reaction flash. A packed reflux column is attached to prevent any loss of chromium. Perchloric acid oxidizes all the chromium to Cr^{+6}. This method was developed by Rains and Menis (RA-155) as a mercury determination procedure. Radian has applied the method to the determination of chromium in NBS standard reference

materials of coal and coal ash and the results were comparable to the reported values.

2.16 Determination of Mercury by Flameless Atomic Absorption

Two methods were used for mercury analysis:

(1) acid permanganate

(2) gold amalgamation

Mercury is determined by a flameless atomic absorption technique. Liquid samples are treated with acid potassium permanganate to oxidize all of the mercury present to the +2 oxidation state. The excess $KMnO_4$ is removed with the addition of hydroxylamine hydrochloride, and the Hg^{+2} is reduced to elemental mercury by the addition of stannous chloride, which is swept through the absorption cell of the atomic absorption unit for determination.

Gold amalgamation collection of mercury has been reported by several workers (KA-086, DI-043). Radian utilizes a double amalgamation technique in which mercury is collected on a gold wire plug in a quartz tube either from flue gas passed through the tube or from thermal desorption into a stream of argon from solid samples. The mercury thus collected is desorbed by heating and amalgamated on a second tube to minimize interferences. Upon desorption from the second tube, the mercury is passed into an absorption cell positioned in the atomic absorption spectrophotometer.

2.17 Sulfur Determination by Titrimetry

The method of sulfur analysis consists of determining the total sulfur as sulfate by titrimetry. Initial sample preparation for coal is performed by ignition in a Parr Ignition Bomb and sorption of the evolved SO_2 in a sodium carbonate solution. Sludge and ash samples are mixed with hydrochloric acid and the solids filtered. In both cases, hydrogen peroxide is added to oxidize sulfite to sulfate. The sample is passed through a cation exchange column to form sulfuric acid. The acid is titrated with standard sodium hydroxide and the sulfur concentration determined.

Nitrate and phosphate ions interfere. Heat applied with hydrochloric acid at pH 2-4 avoids nitrite interference in the column. If the sample is heated at 275°C for 30 minutes to drive off sulfuric acid, phosphate can be determined and the value subtracted from the total to give sulfate ions.

2.18 Spectrophotometric Determination of Boron

Radian's boron procedure combines the separation method of Carlson (CA-084) and the spectrophotometric determination of Mair and Day (MA-190). An ion-exchange column is prepared using a boron specific resin, Amberlite XE-243, to separate boron in the primary digestion from interfering ions and allow complete boron recovery. It is then extracted into chloroform with 2-ethyl-1, 3-hexanediol. Boron in the organic phase is converted to the highly absorbing rosocyanin complex using glacial acetic acid followed by sulfuric acid. The absorbance of the complex is read on a double-beam spectrophotometer and samples compared with a standard calibration curve.

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COAL FIRED POWER PLANT
TRACE ELEMENT STUDY

VOLUME III
STATION II

SEPTEMBER 1975

PREPARED FOR

ENVIRONMENTAL PROTECTION AGENCY
REGION VIII
DENVER, COLORADO

BY

RADIAN CORPORATION
AUSTIN, TEXAS

[redacted] 105

FOREWORD

The four volumes comprising this document describe a coal-fired power plant trace element study prepared under EPA Contract 68-01-2663.

This work was conducted under the direction of Mr. Terry L. Thoem, Project Officer, Environmental Protection Agency, Region VIII, Denver, Colorado. The Radian program staff included Dr. F. G. Mesich as Program Manager and Dr. K. Schwitzgebel as Technical Project Director. Principle contributors were Mr. R. A. Magee, Dr. F. B. Meserole and Mr. R. G. Oldham.

Acknowledgement is given to the station personnel from each utility company whose full cooperation greatly facilitated the field work. Mr. R. M. Mann, Mrs. G. E. Wilkin and Mrs. C. M. Thompson contributed significantly to the program during sampling and analysis.

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VOLUME III

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APPENDIX A - SAMPLING AT STATION II

APPENDIX B - ANALYTICAL PROCEDURES

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TABLE OF CONVERSION UNITS

To Convert From	To	Multiply By
BTU	Calories, kg	0.25198
BTU/pound	Calories, kg/kilogram	0.55552
Cubic feet	Cubic meters	0.028317
Cubic yards	Cubic meters	0.76455
Feet	Meters	0.30480
Feet/second	Meters/second	0.30480
Gallons (U.S. liq.)	Cubic meters	0.0037854
Gallons (U.S. liq.)	Liters	3.7854
Gallons/minute	Cubic meters/minute	0.0037854
Grains/cubic foot	Grams/cubic meter	2.2884
Inches	Centimeters	2.5400
Inches of H_2O (4°C)	Millimeters Hg (0°C)	1.8683
Pounds	Kilograms	0.45359
Pounds/BTU	Kilograms/Calorie, kg	1.8001
Pounds/hour	Kilograms/hour	0.45359
Pounds/standard cubic foot (60°F, 29.92 inches Hg)	Kilograms/standard cubic meter (0°C, 760 mm Hg)	15.155
Tons	Metric tons	0.90719
Yards	Meters	0.9144

STATION II SUMMARY

Station II is representative of a generating station firing sub-bituminous coal and using a hot-side electrostatic precipitator for particulate control. All station streams were sampled and analyzed to determine the trace element content. Material balance closure was achieved for some 23 of the 27 elements characterized in detail. In addition, semi-quantitative results were obtained by spark source mass spectrometry for a total of 53 elements.

Development of correlations permitting the prediction of emissions from coal-fired generating stations will require an extensive data base relating the distribution of trace elements as a function of coal composition and operating conditions. For Station II, the following elements were found to be concentrated in the flue gas emissions over the amount expected from the mass of the ash:

Sulfur
Mercury
Chlorine
Antimony
Chromium
Fluorine
Selenium
Lead
Molybdenum
Nickel
Boron
Zinc
Cadmium

The following elements appear to be uniformly distributed in the ash streams:

Barium
Beryllium
Vanadium
Aluminum
Calcium
Iron
Magnesium
Manganese
Titanium

The elements copper, cobalt, uranium, arsenic, and silver display intermediate behavior and are enriched in the precipitator ash stream.

These results are compared and contrasted in Volume I with Stations I and III using wet scrubbing and mechanical particulate collection, respectively.

1.0 INTRODUCTION

The use of the extensive coal resources in the Northern Great Plains area of the United States may provide a significant part of the country's energy growth for the foreseeable future. As natural gas and oil resources become less available and more costly, coal will receive increasing emphasis as a primary energy source. A coal-fired generating station produces a variety of emissions and effluents ranging from sulfur and nitrogen oxides and particulates in the flue gas to solid and liquid wastes.

In addition to carbonaceous material, coal contains inorganic matter which becomes part of the emissions and effluents from the generating station. The overall objective of this program was to define the sources, levels, and disposition of potentially toxic trace and minor elements in power plant streams. The levels of trace elements in various streams may be expected to be a function of both coal composition and plant operating configuration.

This volume describes the detailed characterization, with respect to trace and minor elements, of a tangentially-fired boiler firing Wyoming sub-bituminous coal and using a hot-side electrostatic precipitator for fly ash control. The particular plant designated as Station II operates at a design rating of 350 MW.

The following trace elements were examined in detail:

Aluminum
Antimony
Arsenic
Barium
Beryllium
Boron
Cadmium
Calcium
Chlorine
Chromium
Cobalt
Copper
Fluorine
Iron
Lead
Magnesium
Manganese
Mercury
Molybdenum
Nickel
Selenium
Silver
Sulfur
Titanium
Uranium
Vanadium
Zinc

A material balance was calculated for each element to provide a sound basis for evaluating the reliability of the emissions measurements. In addition, each sample was surveyed using spark source mass spectrometry to provide a semi-quantitative assessment of 53 trace elements.

The following sections give a description of the plant, a discussion of the sampling, analytical strategies, and presentation and discussion of the experimental data. Appendices are provided which describe the sampling of the plant and analytical methodology.

2.0 SAMPLING AND SAMPLE HANDLING

The procedures used to sample Station II are presented briefly in this section. Details are given in depth in Appendix A, "Sampling at Station II". Sampling was performed during the period October 21-23, 1974.

2.1 Plant Description

Station II consists of a 350 MW unit with a tangentially-fired boiler. The boiler is fired with Wyoming sub-bituminous coal delivered to the plant site by rail and stored in an open pile from which it is conveyed to storage silos. From the silos, the coal is fed to mills for pulverizing prior to delivery to the boiler. Bottom ash, economizer ash and pyrites from the mills are sluiced intermittently to a nearby settling pond using cooling-tower blowdown. Hot-side electrostatic precipitators provide fly ash control. The collected ash is pneumatically conveyed to a storage silo and trucked away from the plant site. Plant load ranged from 335-350 MW during the sampling period.

2.2 Sampling Points and Flow Rate Determinations

The streams sampled are shown schematically in Figure 2-1. The incoming streams are coal and sluice water. Outgoing streams are sluice ash, including pyrites from the mills, discharged sluice water, precipitator ash, and flue gas containing fly ash. The physical location of the points for sampling these streams at the station are schematically shown in Figure 2-2.

Immediately prior to the sampling effort and after the preliminary plant inspection, a special refactory cooling system was installed in the boiler-bottom ash hopper area. Approximately 1.13 x 10^5 lb/hr (225 gpm) of cooling tower blowdown

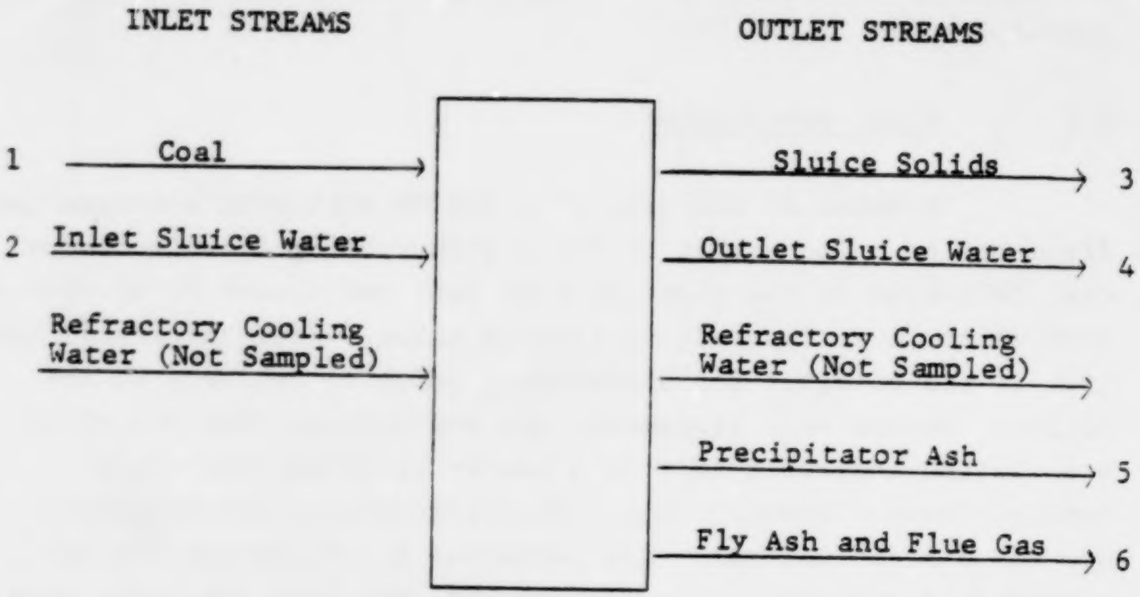
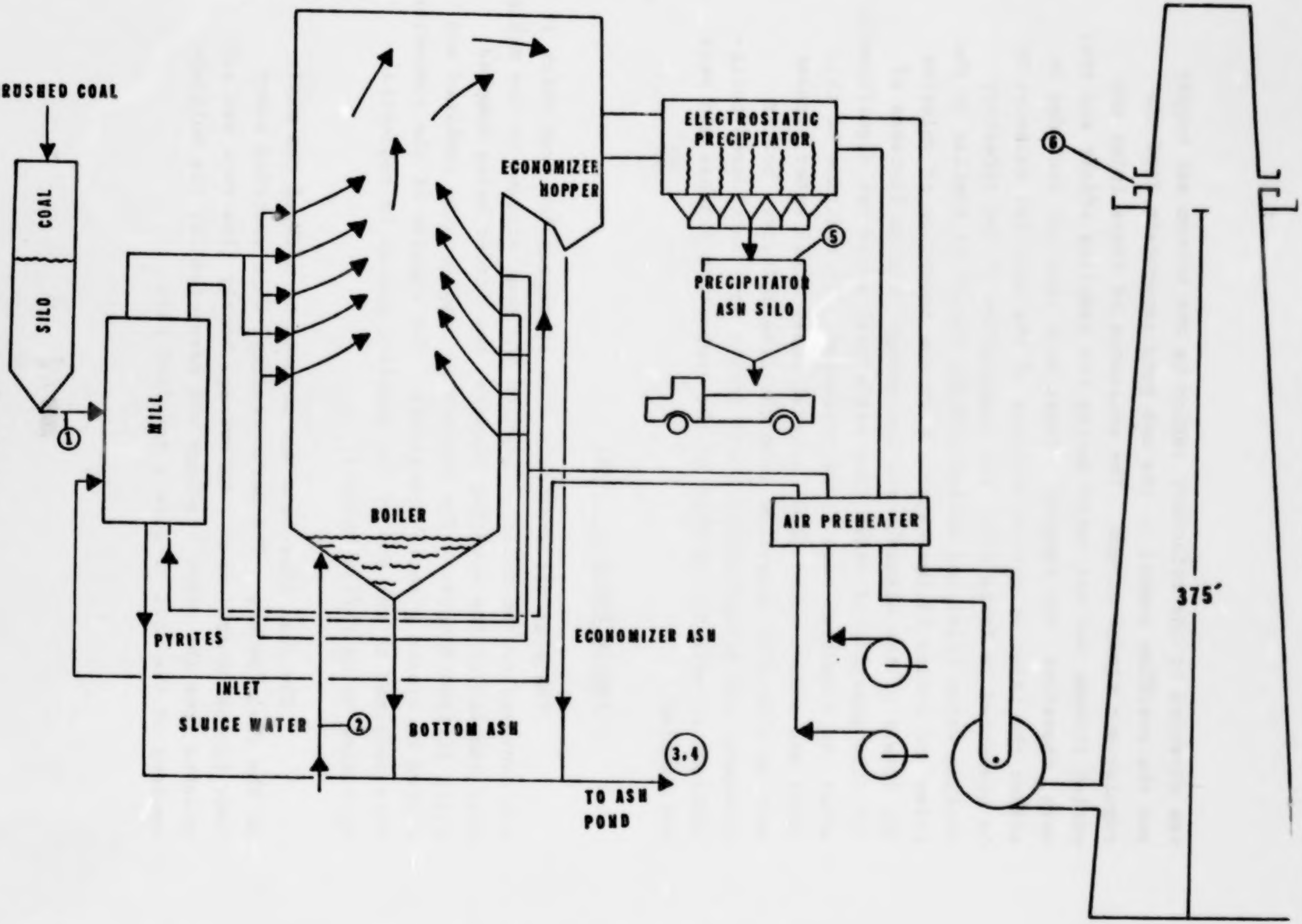

INLET STREAMS
OUTLET STREAMS
1
Coal
2
Inlet Sluice Water
Refractory Cooling Water (Not Sampled)
Sluice Solids
3
Outlet Sluice Water
4
Refractory Cooling Water (Not Sampled)
Precipitator Ash
5
Fly Ash and Flue Gas
6

FIGURE 2-1

INLET AND OUTLET STREAMS
AT STATION II

FIGURE 2-2 SCHEMATIC OF STATION II


CRUSHED COAL
COAL
SILO
①
MILL
PYRITES
INLET
SLUICE WATER
②
BOILER
BOTTOM ASH
ECONOMIZER HOPPER
ECONOMIZER ASH
TO ASH POND
3,4
ELECTROSTATIC PRECIPITATOR
⑤
PRECIPITATOR ASH SILO
AIR PREHEATER
⑥
375'

was directed to the refactory region in the bottom ash hopper and the overflow pumped to the ash pond separately from the regular ash sluice stream. The existence of these inlet and outlet streams was not noted during the sampling effort and they were, therefore, not sampled. These were then not included in either the inlet or outlet portions of the material balances to be presented in Table 4-5. The composition of the refactory cooling water inlet and outlet streams should be similar to the inlet and outlet sluice water. With the exception of chlorine, the levels of the elements are low enough that an increase of 22% (the quantity of water flow neglected) would not significantly alter the elemental mass flows presented. In addition to this inlet and outlet water flow, several other small water streams such as clarifier underflow from the lime softener, boiler blowdown, and miscellaneous plant drains were considered insignificant or were not related to the combustion process and were not sampled.

Sample Point 1: Coal

The coal was stored in five storage silos from which it was conveyed to the mills. Three of the coal streams to the mills were sampled at the metering feeders; one feeder being sampled every fifteen minutes. The individual samples were combined and stored in closed plastic containers. Two samples of the composite were obtained at the end of the sampling period by sequential splitting using riffle buckets.

The coal flow rate was metered to each of the mills at the coal feeders. The meter readings were recorded every hour in the control room. An average hourly flow rate was calculated from the meter readings and corrected for the moisture content of the coal to give a dry feed rate.

Sample Point 2: Inlet Sluice Water

The sluice water was a combination of plant service water, recycle water from the ash pond, and cooling tower blowdown which were combined in a storage tank. Individual samples were collected from the storage tank every three hours and combined to form two composite samples which were acidified to prevent wall adsorption of trace constituents.

The flow rate of sluice water was determined from the pressure drops across the two sluice pumps recorded during the sluicing periods. The intermittent flow rate was averaged over the four-hour sluicing cycle to give an equivalent continuous flow rate.

Sample Points 3 and 4: Ash Sluice

The ash sluice slurry stream was sampled every 2.5 minutes at the point of discharge to the ash pond during the pumping periods which were on a regular four-hour cycle. The combined sluice samples provided a composite sample of bottom ash, economizer ash, and pyrites from the mills. The solids and liquid were separated by filtration. The solids were retained and a portion of the filtrate was acidified to prevent wall adsorption of trace components.

The exit sluice water flow rate was equal to the inlet sluice water rate previously discussed. The ash sluice solids flow rate was calculated from the total ash in the coal, the fly ash discharge (Sample Point 6) and a 78%-22% split between sluice ash and precipitator ash estimated by plant personnel.

Sample Point 5: Precipitator Ash

Samples of the precipitator ash were collected from a portal in the top of the ash storage silo hourly during the sampling period. The individual samples were combined to form a composite sample. Two samples were obtained for analysis by sequential splitting using riffle buckets.

The precipitator ash flow rate was calculated from the estimated split between sluice ash and precipitator ash described above.

Sample Point 6: Flue Gas

The flue gas containing fly ash is discharged from a 500-foot double-walled stack. The stack was equipped with four sampling ports, two at each end of two perpendicular diameters of the stack at the 375-foot level.

The velocity profile in the stack was determined as per EPA Method 2 using S-type pitot tube and thermocouple measurements. Individual values obtained at 16 points in the stack were averaged to determine an integral velocity. The sampling points were located according to EPA Method 1 for sample point location in a circular duct. Sample point location is described in detail in Appendix A.

The dust loadings were measured at the same set of points. Gelman filter devices were used to determine cumulative dust loadings for four points from each sample port. The average grain loading in the stack was then calculated from the individual determinations.

Particulate matter for analysis was collected with wet electrostatic precipitators (WEP). This method of collection permits sampling over an extended time at isokinetic conditions without plugging, as occurs in a filter. Thus, a sufficient quantity of sample can be collected to permit repeated analyses. In addition, problems of trace element contamination by the filter substrate are avoided. A detailed description of the WEP device is given in Appendix A. To confirm the comparibility of this sampling approach with the filter technique recommended by EPA, an EPA filter was run in series with the WEP at Station III. A 125 mm Gelman class "A" glass filter was used in a glass filter holder. The whole assembly was heated to avoid condensation of sulfuric acid mist. The particulate matter collected by the filter during four WEP runs was equivalent to a grain loading of 0.0009 grains/scf. The inlet particulate loading to the WEP was 0.21 grains/scf, giving a collection efficiency of the WEP of 99+%.

The WEP samples were collected at a single point in the stack and a correction made from the grain loading at this point to the average grain loading. The dust concentration at the sampling point was determined from the calcium and titanium concentrations in the WEP sample assuming that these elements are evenly distributed in the particulates with respect to particle size. This assumption is based on work performed by Davison, et al. (DA-105) in which fly ash samples were collected from the duct of a coal-fired station. Andersen impactor samplers were used to separate the particulates into seven size fractions. The results of this work for calcium and titanium are presented in Table 2-1. It is evident from these data that the assumption of uniform ash composition with respect to calcium and titanium holds within experimental limits.

TABLE 2-1

CALCIUM AND TITANIUM ANALYSES* OF ANDERSEN IMPACTOR PARTICLE SIZE FRACTIONS (DA-105)

Particle Diameter μm	Ca wt%	Ti wt%
>11.3	4.9	1.12
7.3 - 11.3	-	-
4.7 - 7.3	4.2	0.92
3.3 - 4.7	-	-
2.06 - 3.3	5.0	1.59
1.06 - 2.06	-	-
0.65 - 1.06	2.6	1.08

* Analysis by X-ray fluorescence spectrometry

The relationship between particle size and titanium and calcium concentrations in the fly ash is important to this correction because the precipitator ash has a larger average particle size than the exiting fly ash. If the titanium and calcium concentrations were dependent on particle size, the assumption made in Equation (2-1) that the titanium and calcium concentrations in the fly ash is the same as in the precipitator ash is not valid.

The point grain loadings were determined from the calcium and titanium concentrations in the WEP samples and the calcium and titanium weight fractions found in the precipitator ash using the relation:

$$\text{Point grain load (gr/scf)} = \frac{15.4\ V_L}{2\ V_G}\left[\frac{XW_L(\text{Ca})}{XW_{Ash}(\text{Ca})} + \frac{XW_L(\text{Ti})}{XW_{Ash}(\text{Ti})}\right] \qquad (2\text{-}1)$$

where,

V_L = volume of the WEP liquor (ml)

V_G = volume of flue gas sampled by WEP (scf)

XW_L(Ca) = concentration of calcium in WEP liquor (μg/ml)

XW_{Ash}(Ca) = weight fraction of calcium in the precipitator ash (ppm)

XW_L(Ti) = concentration of titanium in WEP liquor (μg/ml)

XW_{Ash}(Ti) = weight fraction of titanium in the precipitator ash (ppm)

The point to average grain loading correction factor is then the ratio of the average grain load in the stack to the point grain load calculated from equation (2-1). The correction factor was 1.13.

Gaseous mercury in the flue gas was collected by gold amalgamation. Hydrogen peroxide bubblers were used to absorb SO_2 in the flue gas as per EPA Method 6.

2.3 Summary of Flow Rates and Estimated Errors

A summary of the flow rates is given in Table 2-2. The error limits presented in this table are largely based on Radian field experience and the typical errors expected with the flow measuring devices. The error limits for the sluice water inlet and outlet flows are estimated from the accuracy of the dynamic pressure head measurements and the slope of the pump curves in that region. The error limits for precipitator and sluice ash are based on the assumption that the maximum range around the 22%-78% ash split estimated by plant personnel is between 17%-83% and 27%-73%. Also summarized in this table are the procedures used to obtain the listed rates.

2.4 Sampling Schedule

With the exception of the ash sluice stream, all plant streams were continuous with short residence times in the system. Bottom ash and economizer ash were sluiced on a four-hour cycle and pyrites sluiced every eight hours. Sampling was time-phased to collect samples from the sluice stream representative of the ash which had accumulated during the sampling period.

Sampling was performed during the period October 21-23rd according to the schedule shown in Figure 2-3. Those samples enclosed in parenthesis were analyzed, the rest were retained in reserve.

TABLE 2-2

FLOW RATES FOR STREAMS AROUND STATION II

Stream	Flow Rate	Error Limit	Method Used for Flow Determination
Coal	2.75×10^5 lb/hr	±10%	Metered at coal feeders
Inlet Sluice Water	5.02×10^5 lb/hr	±15%	Pump heads and pump curves
Sluice Solids	4.4×10^3 lb/hr	±25%	Plant personnel estimate of ash distribution and total ash from coal
Sluice Liquid	5.02×10^5 lb/hr	±15%	Rate set equal to inlet sluice water
Precipitator Ash	1.53×10^4 lb/hr.	±10%	Plant personnel estimate of ash distribution and total ash from coal
Flue Gas	5.46×10^7 scfh	±10%	Measured by stack traverses
Fly Ash	1.40×10^2 lb/hr	±10%	Determined from cumulative grain loadings

. point sample

— continuous sampling

	Oct. 21	Oct. 22	Oct. 23
1. Coal Feeder A		......	(..........)
Feeder C		......	(..........)
Feeder E		......	(..........)
2. Inlet Sluice Water		...	(....)
3. Sluice Solids		-	(- -)
4. Outlet Sluice Water		-	(- -)
5. Precipitator Ash		.....	(.........)
6. Flue Gas Velocity	—	— —	— —
7. Flue Gas Particulate Loading	-	— —	— —
8. Flue Gas WEP Particulate Collection		=	(= =)

FIGURE 2-3

SAMPLING SCHEDULE AT STATION II

2.5 Sample Analysis

The techniques used for the quantitative determinations were based on:

(1) atomic absorption
(2) X-ray fluorescence
(3) ion selective electrodes
(4) fluorometry, and
(5) colorimetry

The methods are described in greater detail in Appendix B, "Analytical Procedures".

Figures 2-4 through 2-6 give a brief summary of dissolution and analytical methods used for trace element determination in the samples.

The analytical accuracies of the techniques are summarized in Table 2-3. These values were derived by comparing analytical results with NBS standards where available. In the other cases, recovery studies and/or precision values are the basis for the estimated confidence level.

Semi-quantitative analyses based on spark source mass spectrometry (SSMS) for 53 elements were performed by Accu-Labs, Inc., Denver, Colorado. Since the accuracy of this method is strongly dependent on the matrix, an error limit could not be estimated in the framework of the present study.

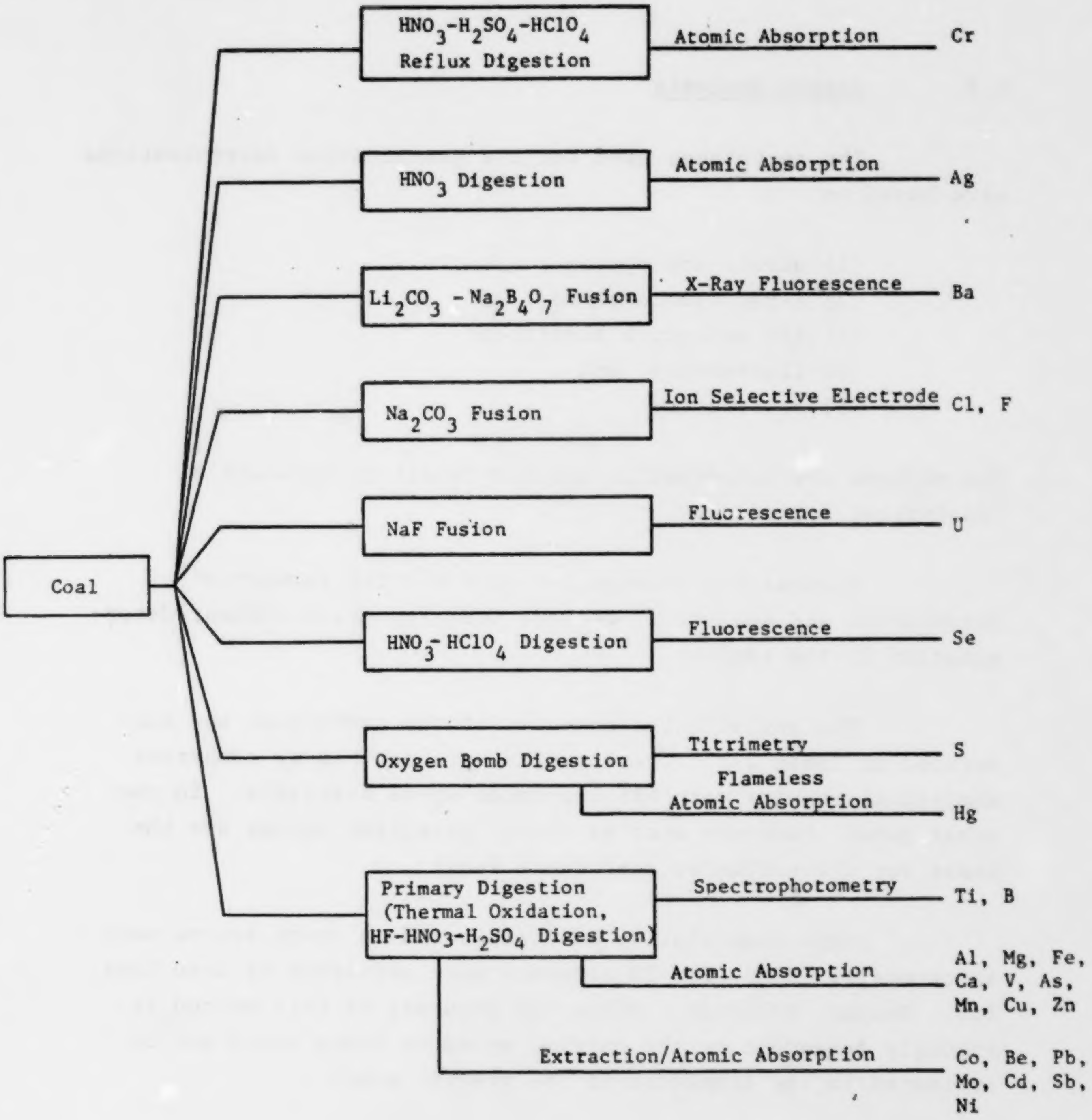

Coal
HNO_3-H_2SO_4-$HClO_4$ Reflux Digestion
Atomic Absorption
Cr
HNO_3 Digestion
Atomic Absorption
Ag
Li_2CO_3 - $Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
Na_2CO_3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO_3- $HClO_4$ Digestion
Fluorescence
Se
Oxygen Bomb Digestion
Titrimetry
S
Flameless Atomic Absorption
Hg
Primary Digestion (Thermal Oxidation, HF-HNO_3-H_2SO_4 Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni

FIGURE 2-1

ANALYSIS PROCEDURE FOR TRACE ELEMENT ANALYSIS OF COAL

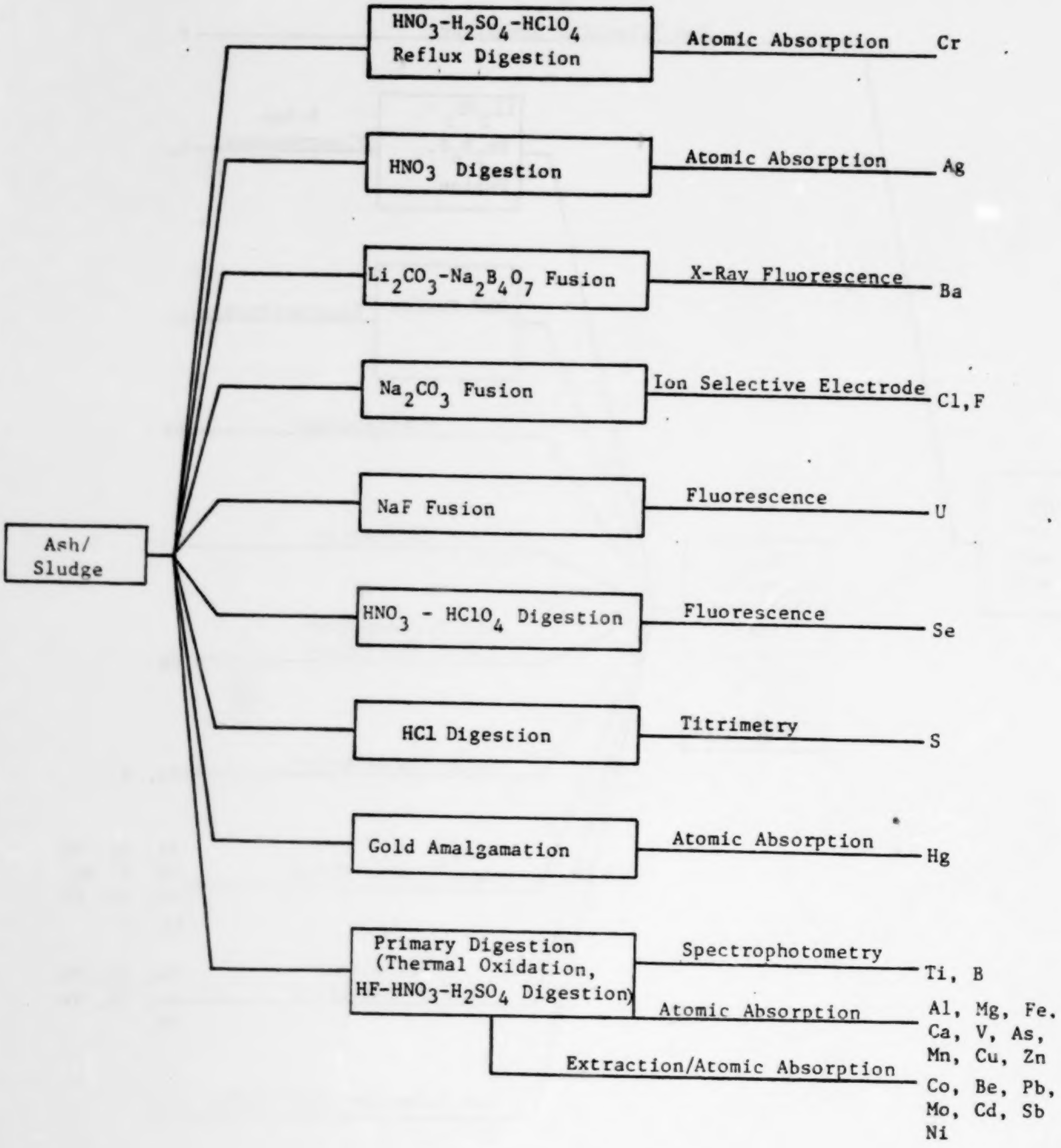

Ash/ Sludge
HNO_3-H_2SO_4-$HClO_4$ Reflux Digestion
Atomic Absorption
Cr
HNO_3 Digestion
Atomic Absorption
Ag
Li_2CO_3-$Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
Na_2CO_3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO_3 - $HClO_4$ Digestion
Fluorescence
Se
HCl Digestion
Titrimetry
S
Gold Amalgamation
Atomic Absorption
Hg
Primary Digestion (Thermal Oxidation, HF-HNO_3-H_2SO_4 Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb Ni

FIGURE 2-2

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS OF COAL ASH AND SLUDGE

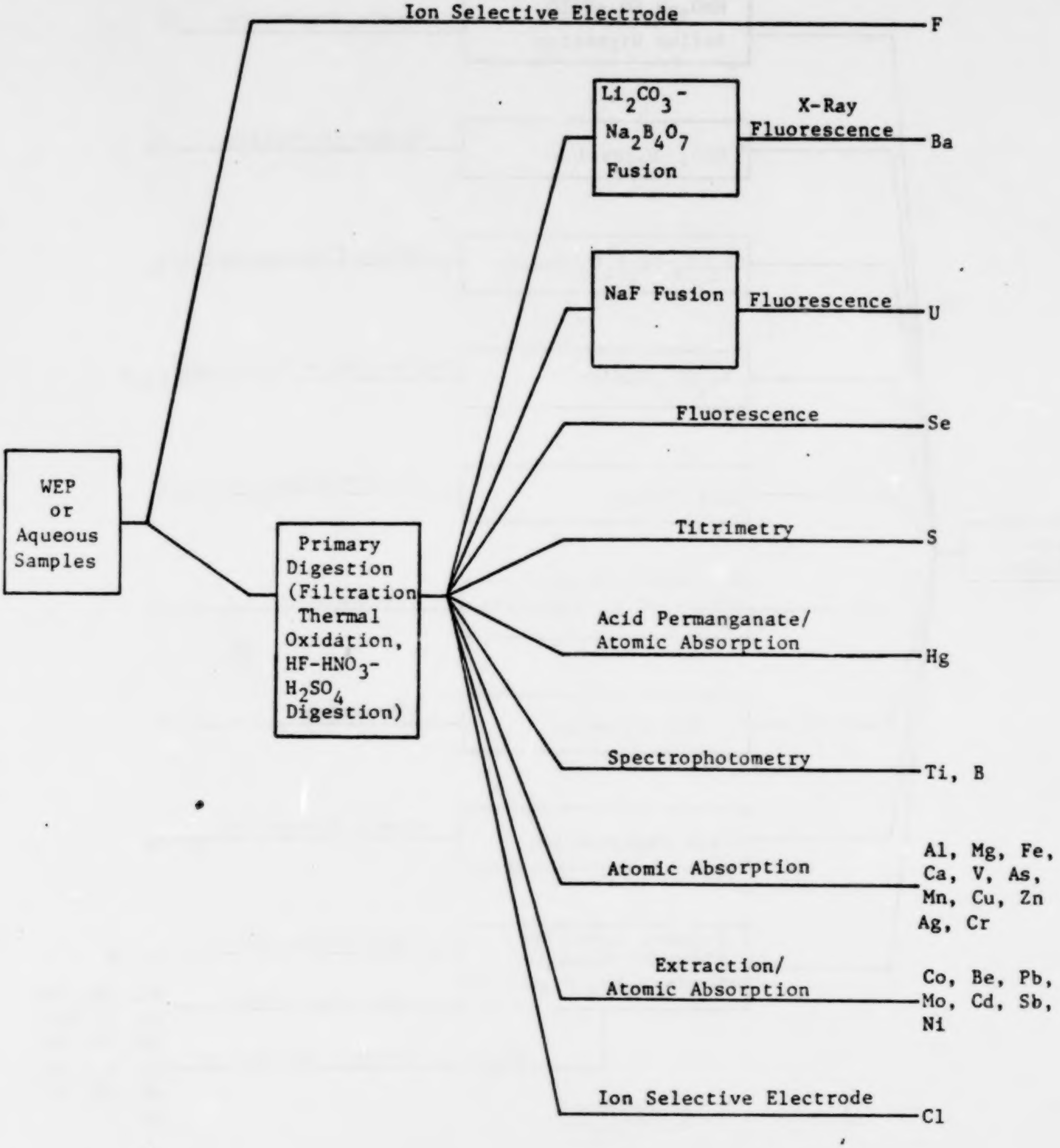

WEP or Aqueous Samples
Ion Selective Electrode
F
Li_2CO_3-$Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
NaF Fusion
Fluorescence
U
Fluorescence
Se
Titrimetry
S
Primary Digestion (Filtration Thermal Oxidation, HF-HNO_3-H_2SO_4 Digestion)
Acid Permanganate/ Atomic Absorption
Hg
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn Ag, Cr
Extraction/ Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni
Ion Selective Electrode
Cl

FIGURE 2-4

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS
OF WET ELECTROSTATIC PRECIPITATOR LIQUORS AND AQUEOUS SAMPLES

TABLE 2-3

ESTIMATED ERROR LIMITS FOR THE CHEMICAL ANALYSES

	WEP Liquor	Aqueous Samples	Coal and Coal Ash
Aluminum	±10%	±10%	± 8 %
Antimony	±10%	±10%	±15 %
Arsenic *	± 8%	± 8%	±10 %
Barium	±20%	±20%	±20 %
Beryllium	±10%	±10%	±12 %
Boron	± 8%	± 8%	± 8 %
Cadmium *	±12%	±12%	±12 %
Calcium	± 2%	± 2%	± 2 %
Chlorine	±10%	±10%	± 8 %
Chromium *	±10%	±10%	±12 %
Cobalt	±10%	±12%	±10 %
Copper *	±10%	±10%	±12 %
Fluorine	± 8%	± 8%	± 8 %
Iron *	± 6%	± 6%	± 6 %
Lead *	±10%	±10%	±18 %
Manganese *	±10%	±10%	± 8 %
Magnesium	± 2%	± 2%	± 2 %
Mercury *	±20%	±10%	±10 %
Molybdenum	±12%	±12%	±15 %
Nickel *	±12%	±12%	±12 %
Selenium *	± 5%	± 5%	± 5 %
Titanium	± 8%	± 8%	± 8 %
Silver	±10%	±10%	±10 %
Sulfur	±10%	± 2%	± 2 %
Uranium *	± 8%	± 8%	± 6 %
Vanadium *	±12%	±12%	±10 %
Zinc *	±10%	±10%	±12 %

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*By comparison with NBS Standard Reference Materials 1633 and 1634.

3.0 DATA EVALUATION

The flow rates and chemical analyses are used to calculate the transport rate of the elements of interest through the boiler and their discharge rates in the effluent streams. A material balance is made around the boiler for each of the elements. The mathematical correlation forms are given in the next sections.

3.1 Trace Element Material Balances

The transport rates of the elements of interest through the steam station are calculated from the chemical analyses of the samples and the flow rates of the incoming and exiting streams. A material balance is calculated for each of the trace elements to verify the determined emission values.

Equating the trace element flow into the system to the flow out of the system gives the following expression:

$$M_c XW_c(j) + M_{asw} XW_{asw}(j) = \qquad (3\text{-}1)$$

$$M_{ss} XW_{ss}(j) + M_{sl} XW_{sl}(j) + M_{pa} XW_{pa}(j) + V_{fg} XV_{fg}(j)$$

where,

M_c = the mass flow rate of coal into the boiler on a dry weight basis (lb/hr)

$XW_c(j)$ = the weight fraction of the element j in the coal on a dry weight basis

M_{asw} = the mass flow rate of the inlet sluice water to the ash sluice system (lb/hr)

$XW_{asw}(j)$ = the weight fraction of the element j in the inlet sluice water

M_{ss} = the mass flow rate of sluice solids from the system (lb/hr)

$XW_{ss}(j)$ = the weight fraction of the element j in the sluice solids

M_{sl} = the discharge rate of sluice water from the ash sluice system equal to M_{asw} (lb/hr)

$XW_{sl}(j)$ = the weight fraction of the element j in the sluice water

M_{pa} = the collection rate of ash in the electrostatic precipitators (lb/hr)

$XW_{pa}(j)$ = the weight fraction of the element j in the precipitator ash

V_{fg} = the volumetric flue gas flow rate in the stack (scfh)

$XV_{fg}(j)$ = the weight of the element j per unit volume of flue gas (lb/scf)

3.2 Error Propagation Analysis

An error propagation analysis was performed on the material balance equations for each element. Error limits are calculated for the total inlet and outlet rates of each element indicating the magnitude of variation to be expected due simply to random errors.

Only errors random in nature are considered in this treatment. A variance is calculated for a given value according to the following standard definition.

$$S^2(Q) = \sum_i^n \left(\frac{\partial Q}{\partial q_i}\right)^2 S^2(q_i) \qquad (3\text{-}2)$$

where

$S(Q)$ = the variance in Q

Q = the material balance value which is a function of the q_i's

q_i = the $i^{\underline{th}}$ independent flow rate or composition used to calculate Q

Confidence intervals can then be assigned to the trace element flow rates calculated for the various streams based on the errors associated with each measurement used in the calculation of these quantities. These limits will be included with the calculated rates discussed in the following section. The error limits for the flow rates were given in Table 2-2 and those assigned to the chemical analyses were listed in Table 2-3 and are in both cases as 2S.

4.0 RESULTS

The values for the proximate and ultimate analysis of the coal are presented in Table 4-1, the coal ash analysis in Table 4-2.

The quantitative analysis results are listed in Table 4-3. The element concentrations in the coal and the flow rates are reported on a dry weight basis. Most of the values in Table 4-3 are presented in parts per million on a weight basis for the solid samples or micrograms per milliliter for liquids. Some elements present in higher concentrations are listed as percent. The WEP results are presented in pounds per standard cubic foot of dry flue gas, where standard conditions are a temperature of 60°F and pressure of 29.92 inches of mercury.

Table 4-4 presents the analytical results obtained by SSMS. The coal sample was analyzed in duplicate to estimate the precision of this method of analysis. The duplicate results differ in some cases by factors of three or greater as indicated for Al, Be, B, Cd, Cl, Eu, Ho, Li, and Nd. Systematic errors caused by matrix effects could not be determined within the scope of the present work. Blind duplicate samples were also submitted for the precipitator ash samples. The differences between duplicate samples were fairly large as evidenced by a factor of 5 for Bi, 3 for Ce, 5 for Dy, 5 for Hf, 3 for I and 3 for Pb. However, these data (SSMS) are useful for order-of-magnitude estimates of trace element flows.

The trace element flow rates in lb/hr are listed in Table 4-5, using the quantitative analysis results and in Table

TABLE 4-1
STATION II COAL ANALYSIS

Proximate		As Received	Dry
% Moisture		29.19	0.00
% Ash		5.12	7.23
% Volatile Matter		30.15	42.58
% Fixed Carbon		35.54	50.19
	Total	100.00	100.00
% Sulfur		0.35	0.49
BTU/lb		8290	11,708
Moisture and Ash Free BTU/lb	12,621		

Ultimate		As Received	Dry
% Carbon		48.31	68.23
% Hydrogen		6.53	4.64
% Nitrogen		0.67	0.95
% Oxygen		39.02	18.46
% Sulfur		0.35	0.49
% Ash		5.12	7.23
	Total	100.00	100.00

TABLE 4-2
STATION II ASH ANALYSIS

Mineral Analysis of Ash	Percent
Silicon Dioxide, SiO_2	28.68
Aluminum Oxide, Al_2O_3	18.25
Titanium Dioxide, TiO_2	1.73
Iron Oxide, Fe_2O_3	4.75
Sodium Oxide, Na_2O	1.32
Potassium Oxide, K_2O	0.40
Calcium Oxide, CaO	21.97
Magnesium Oxide, MgO	3.60
Phosphorus Pentoxide, P_2O_5	1.49
Sulfur Trioxide, SO_3	14.43
Other	3.38
Total	100.00

Ash Viscosity Calculations	
Basic Content	39.69
Acidic Content	60.31
Base-to-Acid Ratio	0.66
Silica-to-Alumina Ratio	1.57
Temperature for 250 Poise Viscosity, $^{\circ}F$	2230

TABLE 4-3 ANALYTICAL RESULTS OF THE STATION II SAMPLES[1]

Element	Coal	Inlet Sluice Water	Precipitator Ash	Sluice Ash	Sluice Ash Filtrate	Combined WEP
Aluminum	.71%	<.1	12%	10.9%	9.2	31.
Antimony	.16	.0023	2.3	<.08	.0038	.0029
Arsenic	2.5	<.0001	48.	1.4	<.0001	.0007
Barium	460.	<.6	.78%	.52%	<.6	.26
Beryllium	.29	<.002	5.6	4.1	<.002	.0042
Boron	31.	.17	550.	240.	.49	.92
Cadmium	<.1	<.002	1.2	<.8	<.002	.0016
Calcium	1.09%	57.	19.5%	15.1%	113.	55.
Chlorine	9.4	8.6	47.	<1.	15.	29.
Chromium	9.3	<.053	116.		<.053	.59
Cobalt	1.5	<.003	27.	18.	<.003	.015
Copper	31.	.012	460.	230.	.022	.12
Fluorine	67.	.45	1130	19.	.70	2.7
Iron	.21%	.12	2.95%	4.06%	.01	9.5
Lead	2.3	.017	22.	11.	.006	.060
Manganese	24.	.034	406.	310.	.016	.18
Magnesium	.15%	15.	2.80%	2.06%	16.	8.1
Mercury	.14	.08	<.010	<.010	<.0004	.017
Molybdenum	.64	<.0002	8.4	3.5	.015	.031
Nickel	2.1	<.02	37.	27.	<.02	.29
Selenium	1.6	.0017	6.8	.35	.0038	.12
Titanium	565.	<.1	.96%	.91%	<.1	2.2
Silver	.048	<.0003	.90	.11	<.0003	.0003
Sulfur	.49%	14.	.80%	910.	108.	2380.
Uranium	.89	.0084	5.8	5.0	.0044	.0031
Vanadium	20.0	0.058	295	190	0.071	.26
Zinc	4.1	.39	77.	156.	.0084	.084

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[1] Values represent the average of duplicate determinations. Values for liquid samples are reported as μg/ml and solids samples as ppm on a dry basis, unless otherwise noted. WEP values are reported as 10^{-8} lb/scf (60°F, 29.92" Hg).

TABLE 4-4 STATION II ANALYTICAL RESULTS BY SS-MS[1]

Element	Coal[2]		Inlet Sluice Water	Precipitator Ash[2]		Sluice Ash	Sluice Ash Filtrate	Combined WEP
Aluminum	670	>.5%	.18	~1%	~7100	>1%	2.5	18
Antimony	.43	.87	.001	2.7	1.1	1.1	.001	<.0007
Arsenic	.89	.98	.004	21	9.1	9.1	.003	<.0016
Barium	400	400	.022	~4900	>.5%	>1%	.22	.66
Beryllium	.32	1.4	--	1.2	.90	2.6	--	<.0007
Bismuth	<.47	<.47	--	12	2.3	5	--	<.0007
Boron	15	53	.016	~1200	~1500	750	.086	.071
Bromine	2.9	6.1	.008	2.8	.73	.73	.018	.0036
Cadmium	5.7	1.7	<.005	14	1.4	1.4	<.005	.0054
Calcium	>1%	>1%	49	>1%	>1%	>1%	100	35
Cerium	5.3	11	--	400	150	530	--	.0073
Cesium	.13	.30	--	.81	.81	.81	--	<.0007
Chlorine	410	89	[3]	47	47	20	[3]	[3]
Chromium	7.4	4.9	.053	61	61	61	.053	.44
Cobalt	3	3	--	16	8.9	14	--	.0054
Copper	25	9.3	.013	250	200	120	.013	.055
Dysprosium	3.7	1.6	--	19	3.7	19	--	<.0007
Erbium	.40	.40	--	2.8	1.2	1.2	--	<.0007
Europium	.39	.12	--	4.8	2.1	4.8	--	<.0007
Fluorine	560	210	[3]	~2100	~2100	210	[3]	[3]
Gadolinium	.13	.13	--	2.1	.75	2.4	--	<.0007
Gallium	1.9	4	--	24	8.7	8.7	.021	.033
Germanium	.37	.22	--	3.6	3	3	.004	.0016
Gold	--	--	--	--	--	--	--	<.0007
Hafnium	1.2	.70	--	6.7	1.3	6.7	--	<.0007
Holmium	.11	.03	--	1.4	.60	1.4	--	<.0007
Iodine	.80	1.6	.001	.3	<.10	.64	.001	<.0007
Iridium	--	--	--	--	--	--	--	<.0007
Iron	~2300	~2300	.17	>1%	>1%	>1%	.53	5.3
Lanthanum	6	2.6	.003	77	42	77	.002	.0054
Lead	13	5.6	.005	120	35	15	.006	.011
Lithium	3.5	17	.009	120	210	120	.002	.0016
Lutetium	<.10	.14	--	.77	.30	.77	--	<.0007
Magnesium	--	>1%	15	>1%	>1%	>1%	16	5.9
Manganese	17	40	.013	250	250	49	.013	.092
Mercury	--	--	--	--	--	--	--	<.0007
Molybdenum	18	7.9	.005	86	30	20	.047	.016
Neodymium	24	4.7	--	250	130	250	--	.011
Nickel	2.2	4.5	.004	98	64	36	.02	.29
Niobium	5.4	2.5	--	32	16	57	--	.0036
Osmium	--	--	--	--	--	--	--	<.0007
Palladium	--	--	--	--	--	--	--	<.0007
Phosphorus	~1300	~1300	.13	>1%	>1%	~4800	.20	4.4
Platinum	--	--	--	--	--	--	--	<.0007

Notes:

[1] Concentration in ppm weight in solids and μg/ml in liquids. WEP analysis in 10^{-8} lb/scf (60°F, 29.92" Hg).
[2] Blind duplicate analysis.
[3] Not recorded due to loss from acidic solution.
[4] Approximate value only due to interference from preservative.
[5] Insufficient sample for determination.
--All elements not reported <0.1 ppm weight in solids or <0.001 μg/ml in liquids.
Maj. - Major component.

TABLE 4-4 STATION II ANALYTICAL RESULTS BY SS-MS[1]

Element	Coal[2]		Inlet Sluice Water	Precipitator Ash[2]		Sluice Ash	Sluice Ash Filtrate	Combined WEP
Potassium	470	280	2.8	~1200	~1200	~1400	4.8	.75
Prascodymium	5.3	5.3	--	40	20	20	--	.0016
Rhenium	--	--	--	--	--	--	--	--
Rhodium	--	--	--	--	--	--	--	<.0007
Rubidium	1.6	.69	.003	43	43	87	.006	.0054
Ruthenium	--	--	--	--	--	--	--	<.0007
Samarium	.67	.33	--	9	1.8	4.2	--	<.0007
Scandium	7.3	7.3	--	40	40	40	--	.0036
Selenium	3.7	1.6	.002	13	4.7	1.3	.009	.040
Silicon	>.5%	>1%	6.1	>1%	>1%	>1%	11	9.2
Silver	<.10	.12	--	.30	.21	.14	<.001	<.0007
Sodium	~2400	>1%	27	>1%	>1%	>1%	43	1.8
Strontium	310	310	2	>.5%	>.5%	>.5%	3.6	1.6
Sulfur	>1%	>1%	~40	--	>1%	>.5%	>100	>82
Tantalum	1	.49	--	6.1	1.3	3	--	<.0007
Tellurium	<.10	<.10	<.001	.93	.13	.16	<.001	.0019
Terbium	<.10	.19	--	2.3	.80	1	--	<.0007
Thallium	<.10	<.10	--	.57	.13	<.10	--	<.0007
Thorium	1.9	4.3	--	24	3.6	18	--	<.0007
Thulium	<.10	.11	--	.3	.14	.70	--	<.0007
Tin	1.6	.73	.006	4.6	2	2.3	.002	.0054
Titanium	600	300	.020	>.5%	>.5%	>1%	.044	1.6
Tungsten	.90	1.5	--	8	3.7	8	--	<.0007
Uranium	2	2	.001	12	2.3	12	<.001	<.0007
Vanadium	40	14	.003	500	210	210	.059	.099
Ytterbium	1	.75	--	5	1.3	2.9	--	<.0007
Yttrium	24	10	--	300	60	160	.002	.082
Zinc	4.9	4.9	.37	110	38	58	.079	.066
Zirconium	16	16	.002	57	31	170	.002	.033

Notes:

[1] Concentration in ppm weight in solids and μg/ml in liquids. WEP analysis in 10^{-8} lb/scf (60°F, 29.92" Hg).
[2] Blind duplicate analysis.
[3] Not recorded due to loss from acidic solution.
[4] Approximate value only due to interference from preservative.
[5] Insufficient sample for determination.
--All elements not reported <0.1 ppm weight in solids or <0.001 μg/ml in liquids.
Maj. - Major component.

TABLE 4-5 STATION II MATERIAL BALANCES*

Element	Coal	Inlet Sluice Water	Σ In	Precipitator Ash	Sluice Ash	Outlet Sluice Water	Flue Gas	Σ Out	Σ Out/Σ In
Aluminum	1950	<.05	1950 ± 250	1830	480	4.6	17	2330 ± 270	1.19
Antimony	.044	.0012	.045 ± .008	.035	<.0004	.0019	.0016	.040 ± .006	.89
Arsenic	.70	<.00005	.7 ± .1	.73	[illegible]	<.00005	.0004	.7 ± .1	1.00
Barium	127	<.30	130 ± 28	119	23	<.30	<.14	140 ± 28	1.08
Beryllium	.080	<.0010	.08 ± .01	.086	.018	<.0010	<.0023	.11 ± .013	1.38
Boron	8.5	.09	8.6 ± 1	8.4	1.1	.25	.50	10 ± 1	1.16
Cadmium	<.028	<.0010	<.029	.018	.0037	<.0010	<.0009	<.024	--
Calcium	3000	29	3030 ± 310	2980	660	57	30	3730 ± 350	1.23
Chlorine	2.6	4.3	6.9 ± .8	.72	<.004	7.5	16	25 ± 3	3.62
Chromium	2.5	<.027	2.6 ± .4	1.8	.34	<.027	.32	2.5 ± .3	.96
Cobalt	.41	<.0015	.41 ± .06	.41	.079	<.0015	.0081	.5 ± .06	1.22
Copper	8.5	.0060	8.5 ± 1	7.0	1.0	.011	.068	8 ± 1	.94
Fluorine	18	.23	19 ± 2	17	.084	.35	1.5	19 ± 2	1.00
Iron	580	.060	580 ± 70	450	180	.0050	5.2	640 ± 70	1.10
Lead	.63	.0085	.64 ± .13	.34	.048	.0030	.033	.42 ± .07	.66
Magnesium	413	7.4	420 ± 40	428	91	7.9	4.4	530 ± 50	1.26
Manganese	6.6	.017	6.6 ± .8	6.2	1.4	.0080	.10	7.7 ± .9	1.17
Mercury	.037	.040	.077 ± .009	<.0002	<.00004	<.0002	.0093	.010 ± .002	.13
Molybdenum	.18	<.0001	.18 ± .03	.13	.015	.0075	.017	.17 ± .02	.94
Nickel	.58	<.010	.59 ± .09	.57	.12	<.010	.16	.86 ± .1	1.46
Selenium	.44	.0009	.44 ± .05	.10	.0015	.0019	.068	.17 ± .01	.39
Silver	.013	<.0001	.013 ± .002	.014	.0005	<.0001	.0002	.015 ± .002	1.15
Sulfur	1350	7	1350 ± 140	120	4.0	54	1300	1480 ± 180	1.10
Titanium	160	<.05	160 ± 20	146	40	<.05	1.2	190 ± 20	1.19
Uranium	.24	.0042	.25 ± .03	.089	.022	.0022	.0017	.11 ± .01	.44
Vanadium	5.5	.029	5.5 ± .8	4.5	.84	.036	.14	5.5 ± .7	1.00
Zinc	1.1	.20	1.3 ± .2	1.2	.69	.0042	.046	1.9 ± .3	1.46

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*All values in lb/hr.

4-6, using the SSMS results. The sum of the elemental flow rates of all incoming streams, coal and ash sluice water, are given as Σ In. The flow rates of the outgoing streams, sluice ash, sluice ash filtrate, precipitator ash and flue gas, also were added and are listed as Σ Out. The error limits given were calculated from the estimated errors in the analyses and in the flows according to the procedures described in Section 3.0.

The emission results for sulfur and particulates are summarized in Table 4-7 since these are the two emission parameters of greatest immediate importance. The results are provided on a lb/BTU basis to facilitate comparison to other stations.

TABLE 4-6 STATION II MATERIAL BALANCE BASED ON
SPARK SOURCE MASS SPECTROGRAPHIC DATA *

Element	Coal	Inlet Sluice Water	Σ In	Precipitator Ash	Sluice Ash	Sluice Ash Filtrate	WEP	Σ Out
Aluminum	>1375	.090	>1400	>162	>46	1.3	9.9	>220
Antimony	.17	.0005	.17	.31	.005	.0005	<.0004	.037
Arsenic	26	.002	26	.24	.042	.002	<.0009	.29
Barium	110	.011	110	~79	>46	.11	.36	>126
Beryllium	.25	<.0005	.25	.018	.012	<.0005	<.0004	.031
Bismuth	<.13	<.0005	<.13	.12	.023	<.0005	<.0004	.14
Boron	9.4	.008	9.4	~23	3.5	.043	.039	~26
Bromine	1.2	.004	1.2	.029	.003	.009	.002	.043
Cadmium	1.0	<.003	1.0	.12	.006	<.003	.003	.14
Calcium	>2750	25	>2800	>162	>46	50	19	>280
Cerium	2.3	<.0005	2.3	4.5	2.4	<.0005	.004	6.9
Cesium	.061	<.0005	.061	.013	.004	<.0005	<.0004	.018
Chlorine	69	--	69	.76	.092	--	--	.85
Chromium	1.7	.027	1.7	.99	.28	.027	.24	1.5
Cobalt	.83	<.0005	.83	.21	.065	<.0005	.003	.28
Copper	4.7	.007	4.7	3.6	.55	.007	.030	4.2
Dysprosium	.74	<.0005	.74	.18	.088	<.0005	<.0004	.27
Erbium	.11	<.0005	.11	.032	.006	<.0005	<.0004	.039
Europium	.072	<.0005	.072	.057	.022	<.0005	<.0004	.080
Fluorine	106	--	106	~34	.97	--	--	~35
Gadolinium	.036	<.0005	.036	.023	.011	<.0005	<.0004	.035
Gallium	.83	<.0005	.83	.26	.040	.011	.018	.33
Germanium	.083	<.0005	.083	.053	.014	.002	.0009	.070
Gold	<.028	<.0005	<.028	<.002	<.0004	<.0005	<.0004	<.003
Hafnium	.28	<.0005	.28	.065	.031	<.0005	<.0004	.097
Holmium	.019	<.0005	.020	.016	.006	<.0005	<.0004	.024
Iodine	.33	.0005	.33	.005	.003	<.0005	<.0004	.009
Iridium	<.028	<.0005	<.028	<.002	<.0004	<.0005	<.0004	<.003
Iron	~633	.085	~630	>162	>46	.27	2.9	>210
Lanthanum	1.2	.002	1.2	.97	.35	.001	.003	1.3
Lead	2.6	.003	2.6	1.2	.069	.003	.006	1.3
Lithium	2.8	.005	2.8	2.7	.55	.001	.0009	3.2
Lutetium	.039	<.0005	.039	.009	.004	<.0005	<.0004	.013
Magnesium	>2750	7.5	>2800	>162	>46	8.0	3.2	>220
Manganese	8.0	.007	8.0	4.1	.23	.007	.050	4.3
Mercury	<.028	<.0005	<.028	<.002	<.0004	<.0005	<.0004	<.003

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*All values in lb/hr.

TABLE 4-6 STATION II MATERIAL BALANCE BASED ON
SPARK SOURCE MASS SPECTROGRAPHIC DATA (Cont'd)*

Element	Coal	Inlet Sluice Water	Σ In	Precipitator Ash	Sluice Ash	Sluice Ash Filtrate	WEP	Σ Out
Molybdenum	3.6	.003	3.6	.94	.092	.024	.009	1.1
Neodymium	4.0	<.0005	4.0	3.1	1.2	.0005	.006	4.2
Nickel	.94	.002	.94	1.3	.17	.010	.16	1.6
Niobium	1.1	<.0005	1.1	.39	.26	<.0005	.002	.65
Osmium	<.028	<.0005	<.028	<.002	<.0004	<.0005	<.0004	<.003
Palladium	<.028	<.0005	<.028	<.002	<.0004	<.0005	<.0004	<.003
Phosphorus	~358	.065	~358	>162	~22	.10	2.4	>187
Platinum	<.028	<.0005	<.028	<.002	<.0004	<.0005	<.0004	<.003
Potassium	99	1.4	100	~19	~6.5	2.4	.41	~29
Praseodymium	1.5	<.0005	1.5	.49	.092	<.0005	.0009	.58
Rhenium	<.028	--	<.028	<.002	<.0004	--	<.0004	<.002
Rhodium	<.028	<.0005	<.028	<.002	<.0004	<.0005	<.0004	<.003
Rubidium	.33	.002	.33	.70	.40	.003	.003	1.1
Ruthenium	<.028	<.0005	<.028	<.002	<.0004	<.0005	<.0004	<.003
Samarium	.14	<.0005	.14	.087	.019	<.0005	<.0004	.11
Scandium	2.0	<.0005	2.0	.65	.18	<.0005	.002	.84
Selenium	.74	.001	.74	.14	.006	.005	.022	.18
Silicon	>2750	3.1	>2800	>162	>46	5.5	5.0	>220
Silver	.033	<.0005	.034	.004	.0006	<.0005	<.0004	.006
Sodium	>2750	14	>2800	>162	>46	22	1.0	>230
Strontium	85	1.0	86	>81	>23	1.8	.90	>107
Sulfur	>2750	~20	>2800	>162	>23	>50	~45	~280
Tantalum	.22	<.0005	.22	.060	.014	<.0005	<.0004	.075
Tellurium	<.028	<.0005	<.028	.009	.000	<.0005	.001	.011
Terbium	.052	<.0005	.053	.024	.005	<.0005	<.0004	.030
Thallium	<.028	<.0005	<.028	.006	<.0004	<.0005	<.0004	.007
Thorium	.85	<.0005	.85	.22	.083	<.0005	<.0004	.31
Thulium	.030	<.0005	.031	.004	.003	<.0005	<.0004	.008
Tin	.33	.003	.33	.053	.011	.001	.003	.068
Titanium	124	.010	124	>81	>46	.022	.90	>128
Tungsten	.33	<.0005	.33	.096	.037	<.0005	<.0004	.13
Uranium	.55	.0005	.55	.12	.055	<.0005	<.0004	.17
Vanadium	7.4	.002	7.4	5.8	.97	.030	.054	6.8
Ytterbium	.24	<.0005	.24	.052	.013	<.0005	<.0004	.066
Yttrium	4.7	.0005	4.7	2.9	.74	.001	.045	3.7
Zinc	1.3	.19	1.5	1.2	.27	.040	.036	1.5
Zirconium	4.4	.001	4.4	.71	.78	.001	.018	1.5

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*All values in lb/hr.

TABLE 4-7

EMISSION RESULTS FOR PARTICULATES AND SULFUR DIOXIDE AT STATION II

	Particulates (Ash)	Sulfur Dioxide
Concentration in flue gas	0.018 gr/scf	280 ppm (v/v)
Quantity in coal per unit heat value	6.18 lb/10^5 BTU	0.84 lb/10^6 BTU
Emissions in flue gas per unit heat value of coal burned	0.044 lb/10^6 BTU	0.81 lb/10^6 BTU

5.0 DISCUSSION OF RESULTS

The results given in Section 4.0 can be used to establish the distribution of each trace element in the station exit streams. The degree of closure of the individual element material balances provides a measure of the overall reliability of the results.

5.1 Material Balance Closure

Closure of the balances within error limits indicates a high reliability for the emissions measurements. Closure within the error limits is indicated by an overlap of the error bands for Σ In and Σ Out presented in Table 4-5. Some 23 elements closed within error limits:

Aluminum
Antimony
Arsenic
Barium
Beryllium
Boron
Cadmium
Calcium
Chromium
Cobalt
Copper
Fluorine
Iron
Lead
Magnesium
Manganese
Molybdenum
Nickel
Silver
Sulfur
Titanium
Vanadium
Zinc

The balances were outside the error limits for chlorine, mercury, selenium, and uranium. The degree of closure is as follows:

Chlorine	6.9 ± .7 lb/hr in	25 ± 3 lb/hr out
Mercury	.077 ± .008 lb/hr in	.010 ± .002 lb/hr out
Selenium	.44 ± .05 lb/hr in	.18 ± .02 lb/hr out
Uranium	.25 ± .03 lb/hr in	.12 ± .02 lb/hr out

These discrepancies must be attributed to random errors in sampling, sample handling and/or analysis. Sampling is a particular problem for chlorine, mercury and selenium which may be present in the vapor state.

The degree of balance closure obtained by the quantitative analyses and by the spark source emission spectrometry method are compared in Table 5-1. A normalized deviation was calculated for each element according to:

$$\mathrm{ND}(j) = \frac{\Sigma \mathrm{in}(j) - \Sigma \mathrm{out}(j)}{(\Sigma \mathrm{in}(j) + \Sigma \mathrm{out}(j))/2} \qquad (5\text{-}1)$$

The average of the normalized deviations is 0.007 for the quantitative procedures and +0.89 for the SSMS method. A negative average indicates some systematic bias toward the outlet flowrates and a positive average indicates bias toward the inlet streams. The root mean square of the normalized deviations according to:

$$\mathrm{RMS}_{\mathrm{ND}} = \left[\frac{1}{n} \sum_{j} \left(\frac{\Sigma \mathrm{in}(j) - \Sigma \mathrm{out}(j)}{\frac{\Sigma \mathrm{in}(j) + \Sigma \mathrm{out}(j)}{2}} \right)^{2} \right]^{\frac{1}{2}} \qquad (5\text{-}2)$$

is 0.46 for the quantitative methods and 1.18 for SSMS. These provide some measure of the overall material balance closure for each of the two analytical approaches.

The average of the ND values for 53 entries based on SSMS results is 0.66 and the RMS equals 0.99. Results less than or greater than a certain value were considered inconclusive and not included in these calculations.

TABLE 5-1
DEVIATIONS FROM MATERIAL BALANCE CLOSURE FOR QUANTITATIVE ANALYSES AND SPARK SOURCE MASS SPECTROMETRIC ANALYSES FOR STATION II

Elements	Quantitative Normalized[1] Deviation	SSMS Normalized[1] Deviation
Aluminum	-0.18	1.46
Antimony	0.12	1.29
Arsenic	0	1.96
Barium	-0.07	-0.14
Beryllium	-0.32	1.56
Boron	-0.15	-0.94
Cadmium	0.19	1.51
Calcium	-0.21	1.64
Chlorine	-1.1	1.95
Chromium	0.04	0.13
Cobalt	-0.20	0.99
Copper	0.06	0.11
Fluorine	0	1.01
Iron	-0.10	1.00
Lead	0.42	0.67
Magnesium	-0.23	1.71
Manganese	-0.15	0.60
Mercury	1.5	1.61
Molybdenum	0.06	1.06
Nickel	-0.37	-0.52
Selenium	0.88	1.22
Silver	-0.14	1.40
Sulfur	-0.09	1.64
Titanium	-0.17	-0.03
Uranium	0.77	1.06
Vanadium	0	0.08
Zinc	-0.38	0
Average of Normalized Deviations	0.007	0.89
RMS of Deviations[2]	0.46	1.18

NOTES:

1. Normalized Deviation = $\dfrac{\Sigma_{in}(j) - \Sigma_{out}(j)}{\left(\dfrac{\Sigma_{in}(j) + \Sigma_{out}(j)}{2}\right)}$

2. Root Mean Square of Normalized Deviations = $\sqrt{\dfrac{\sum_j \left[\dfrac{\Sigma_{in}(j) - \Sigma_{out}(j)}{\left(\dfrac{\Sigma_{in}(j) + \Sigma_{out}(j)}{2}\right)}\right]^2}{n}}$

5.2 Distribution of Elements in the Exit Streams

The coal ash was distributed among the exit streams as follows:

Sluice ash	22.2%
Precipitator ash	77.1%
Flue gas	0.7%

The sluice ash is the sum of bottom ash, economizer ash and pyrites originating from the mills. The degree of leaching of the elements during the sluice operation was calculated from the concentration increase of an element in the exit sluice water stream compared to the inlet sluice water. The increase in the exit water stream was added to the value of the elements in the total sluice ash. These corrections were negligible with the exceptions of antimony, calcium, chlorine, fluorine, selenium, and sulfur.

The distribution of the individual elements is shown in Table 5-2. Values greater than 22.2% in the sluice ash, greater than 77.1% in the precipitator ash and greater than 0.7% in the flue gas indicate enrichments of the element in the corresponding stream; values smaller than these numbers indicate a depletion. The total amount of an incoming element in the coal in pounds per hour is also shown in this table.

The results of these distributions are graphically shown in Figure 5-1. The average amount of sluice ash, precipitator ash and flue gas plus fly ash are represented as green, blue and red vertical lines respectively. The distribution of an element within these streams is shown as green (sluice ash), blue (precipitator ash) and red (flue gas and fly ash) horizontal lines. Crossing of a horizontal and vertical line of the

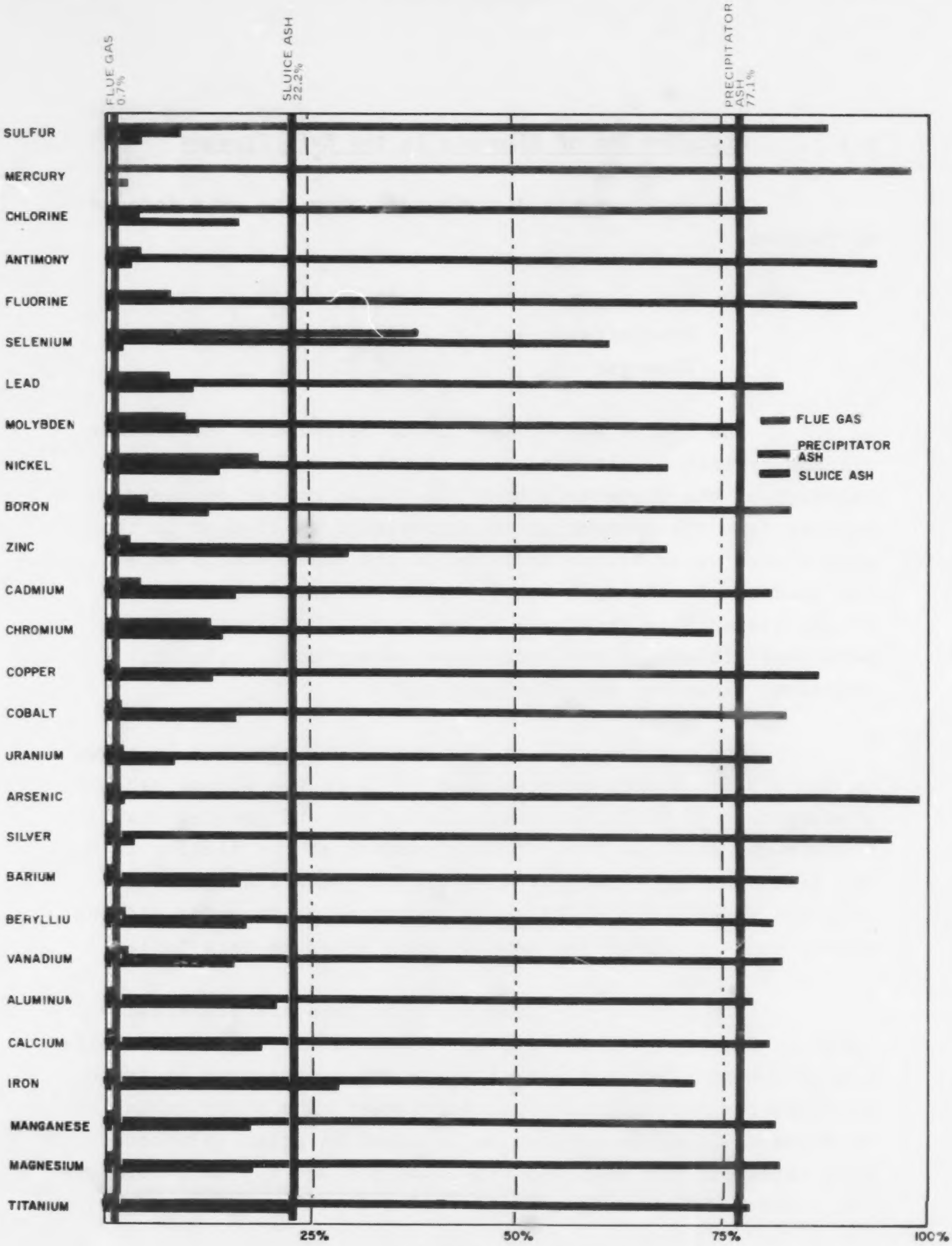

FIGURE 5.1
DISTRIBUTION OF ELEMENTS AMONG SLUICE ASH, PRECIPITATOR ASH, AND FLUE GAS AT STATION II

150 [redacted]

TABLE 5-2

DISTRIBUTION OF ELEMENTS AMONG SLUICE ASH, PRECIPITATOR ASH, AND FLUE GAS AT STATION II

Elements	Coal in lb/hr	Sluice Ash (Average 22.2%)	Precipitator Ash (Average 77.1%)	Flue Gas (Average 0.7%)
Aluminum	1950	20.5	78.8	0.7
Antimony	0.044	2.7	93.4	3.9
Arsenic	0.70	0.8	99.1	0.05
Barium	127	16.0	83.9	<0.09
Beryllium	0.080	16.9	81.0	<2.0
Boron	8.5	12.1	83.2	4.7
Cadmium	<0.028	<15.7	80.5	<3.8
Calcium	3000	18.5	80.7	0.8
Chlorine	2.6	16.0	3.8	80.2
Chromium	2.5	13.9	73.7	12.4
Cobalt	0.41	15.6	82.9	1.5
Copper	8.5	12.7	86.5	0.8
Fluorine	18	1.1	91.3	7.6
Iron	578	27.9	71.3	0.8
Lead	0.63	10.3	82.2	7.5
Magnesium	413	17.2	82.0	0.8
Manganese	6.6	17.3	81.5	1.2
Mercury	0.037	2.1	0	97.9
Molybdenum	0.18	12.8	77.8	9.4
Nickel	0.58	13.6	68.2	18.2
Selenium	0.44	1.4	60.9	37.7
Silver	0.013	3.2	95.5	1.3
Sulfur	1350	3.4	8.8	87.8
Titanium	155	21.1	78.3	0.6
Uranium	0.24	18.0	80.5	1.5
Vanadium	5.5	15.3	82.3	2.4
Zinc	1.1	29.4	68.0	2.6

same color indicates enrichment of an element in the corresponding exit stream. The contrary indicates a depletion.

The elements can be divided into three broad classes. The first class includes those elements enriched in flue gas plus fly ash. Elements belonging to this group are:

Sulfur
Mercury
Chlorine
Antimony
Chromium
Fluorine
Selenium
Lead
Molybdenum
Nickel
Boron
Zinc
Cadmium

The material balances for chlorine, mercury, and selenium were outside error limits; therefore, the exact magnitude of the enrichment in these cases may be uncertain, but the general trend is evident.

The following elements, class two, are depleted in the bottom ash and preferably enriched in the precipitator ash.

Copper
Cobalt
Uranium
Arsenic
Silver

Only the balance for uranium failed to close for these elements.

Elements belonging to class three show normal distribution in the exit streams. These are:

Barium
Beryllium
Aluminum
Calcium
Vanadium
Iron
Magnesium
Manganese
Titanium

Although a detailed investigation of the mechanisms of enrichment for the trace elements in a given stream is beyond the scope of this study, several general comments can be made.

Enrichment in the precipitator ash or flue gas is expected in those cases for which:

(1) species are partly or completely evaporated at the boiler temperature

(2) species change to other compounds within the boiler atmosphere with subsequent volatilization.

The volatilized species can subsequently

(1) leave the plant in the vapor state,

(2) partly recondense, or

(3) recondense completely on the available particulate surface area.

In the last two cases, enrichment in the exit flue gas and the precipitator ash will be observed; in the first case, enrichment in the flue gas is observed with depletion in the bottom ash and precipitator ash. Sulfur, mercury and chlorine are good examples for this behavior. The evaporation-recondensation mechanism will lead to a concentration dependence as function of particle size.

APPENDIX A

SAMPLING AT STATION II

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APPENDIX A
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1.0 INTRODUCTION

Sampling at Station II was performed by Radian personnel during the period of October 21-23, 1974. Station II was selected as part of the Northern Great Plains Resources Program trace elements study to be representative of a plant with hot-side electrostatic precipitator for fly ash control.

Representative samples of all inlet and outlet streams around the power plant were collected with the objective of quantifying the trace element emissions from the plant. Analyses of the samples for the trace elements of interest in combination with flow rate data for each stream during the sample period allows a material balance to be performed for each element around the plant. These material balances serve two main functions: (1) closure of the material balances lends credibility to the sampling and analytical techniques and, therefore, to the emission data produced, and (2) data is generated which allows the ultimate fate of individual trace elements to be determined and their flow through the plant to be traced.

The following sections provide descriptions of the station, the sampling techniques utilized, and the flow rate measurements performed.

2.0 PLANT DESCRIPTION

Station II consists of one 350 MW tangentially-fired boiler. A second boiler, essentially identical to the first, is presently under construction. Hot-side electrostatic precipitators designed for 350 MW at an inlet gas temperature of 828°F are used for fly ash control. The boiler is fired with sub-bituminous coal transported by rail from Wyoming, where it is strip-mined. The coal typically contains 30% moisture, 5% ash, 0.5% sulfur, and 33% volatile matter and has a heating value of 8400 BTU/lb. The coal is initially stored in an open pile from which it is conveyed to five storage silos. From the storage silos the coal is fed to the mills where it is pulverized prior to delivery to the boiler through a pneumatic conveyer system.

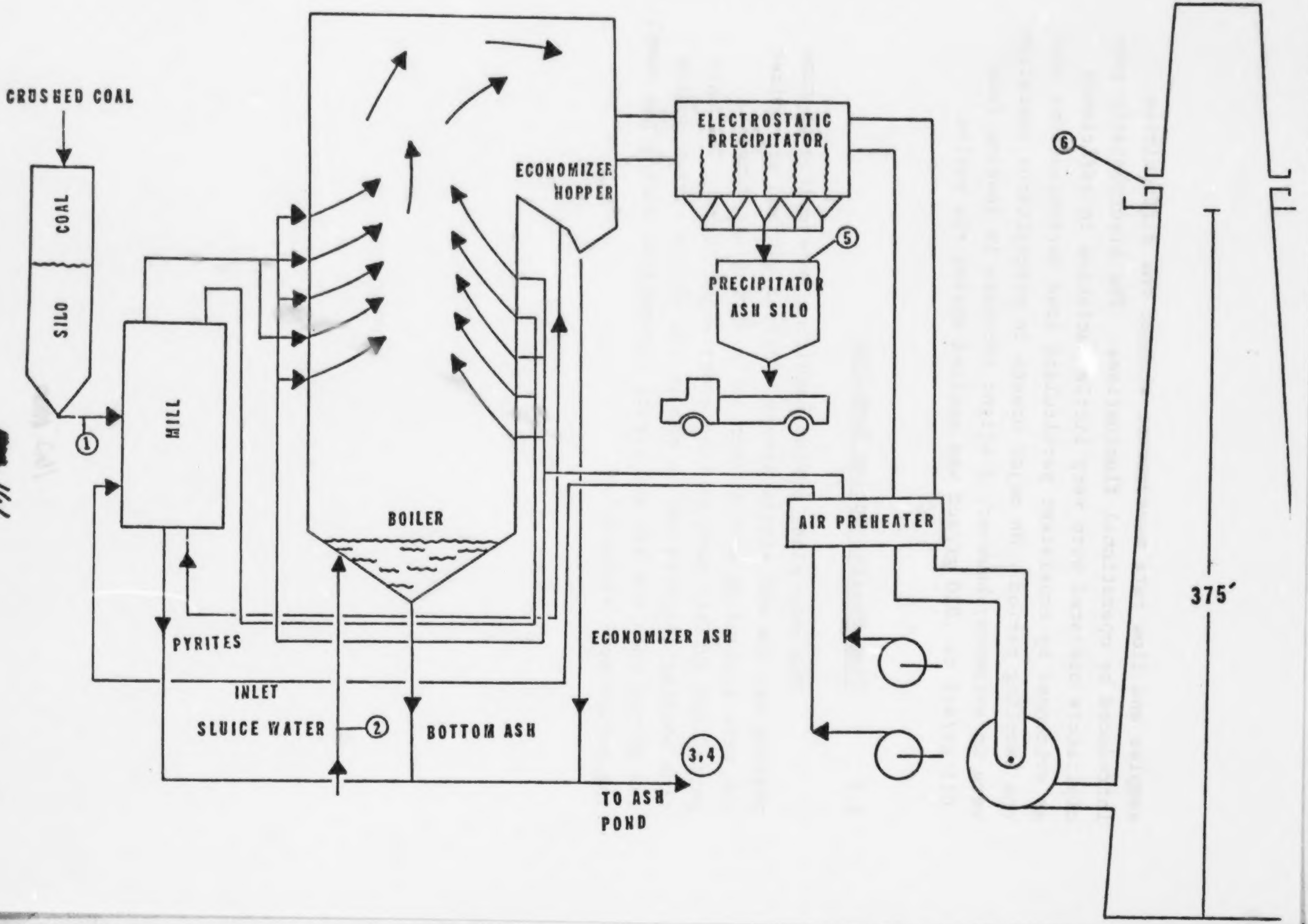
Pyrites from the mills, economizer ash, and bottom ash are sluiced alternately to an ash pond at approximately four hour intervals. The ash collected in the electrostatic precipitators is transferred to an ash storage silo by a pneumatic conveyer system and removed from the plant site by truck. Flue gas exits the system through a 500 ft. stack, approximately 25 ft. in diameter.

A schematic of the station with all sampled streams is presented in Figure 2-1.

2.1 Plant Operation During Sampling

During the period of sampling the plant load varied between 335 and 350 MW. This consistency of operation provided very steady conditions allowing collection of representative

FIGURE 2-1 SCHEMATIC OF STATION II


CRUSHED COAL
COAL
SILO
①
MILL
PYRITES
INLET
SLUICE WATER
②
BOILER
BOTTOM ASH
ECONOMIZER HOPPER
ECONOMIZER ASH
③,④
TO ASH POND
ELECTROSTATIC PRECIPITATOR
⑤
PRECIPITATOR ASH SILO
AIR PREHEATER
⑥
375'

samples and flow rate measurement without the difficulties introduced by operational fluctuations. The electrostatic precipitators operated with very little variation in efficiency as evidenced by consistent particulate load determinations over the sampling period. No major upsets in precipitator operation were in evidence; however, a slight increase in loading from .015 gr/scf to .020 gr/scf was noticed during the period.

2.2 Time Phasing During Sampling

The only plant stream requiring some degree of time phasing was the ash sluice stream. Bottom ash and economizer ash were sluiced on a four hour cycle during the sampling period and pyrites were sluiced every eight hours. The only time phasing required was to sample the sluice stream during the period when the ash and pyrite accumulated during the sampling period were sluiced.

3.0 DESCRIPTION OF SAMPLING POINTS

The sample point locations are indicated schematically in Figure 2-1 and the process streams are summarized schematically in Figure 3-1. The following sections provide detailed descriptions of the sample points and the techniques employed to obtain samples representative of the streams during the sampling period. All samples were collected both during a preliminary sampling on October 22nd and the primary sampling on October 23rd.

Immediately prior to the sampling effort and after the preliminary plant inspection, a special refactory cooling system was installed in the boiler-bottom ash hopper area. Approximately 1.13 x 10^5 lb/hr (225 gpm) of cooling tower blowdown was directed to the refactory region in the bottom ash hopper and the overflow pumped to the ash pond separately from the regular ash sluice stream. The existence of these inlet and outlet streams was not noted during the sampling effort and they were, therefore, not sampled. These were then not included in either the inlet or outlet portions of the material balances to be presented in Table 4-5. The composition of the refactory cooling water inlet and outlet streams should be similar to the inlet and outlet sluice water. With the exception of chlorine, the levels of the elements are low enough that an increase of 22% (the quantity of water flow neglected) would not significantly alter the elemental mass flows presented. In addition to this inlet and outlet water flow, several other small water streams such as clarifier underflow from the lime softener, boiler blowdown, and miscellaneous plant drains were considered insignificant or were not related to the combustion process and were not sampled.

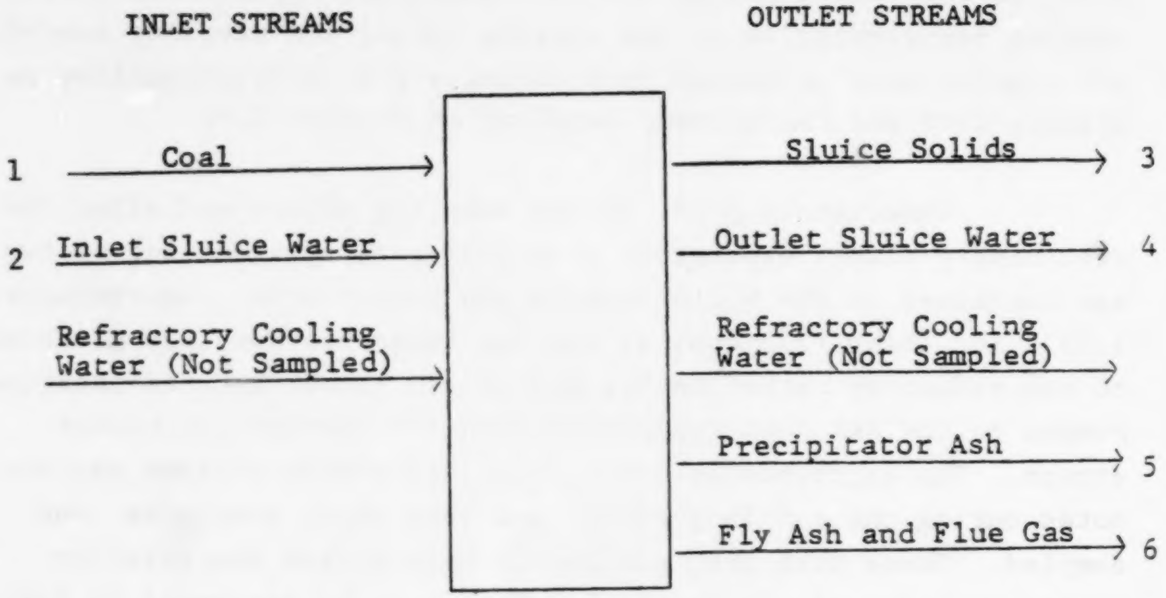

INLET STREAMS
OUTLET STREAMS
1
Coal
2
Inlet Sluice Water
Refractory Cooling Water (Not Sampled)
Sluice Solids
3
Outlet Sluice Water
4
Refractory Cooling Water (Not Sampled)
Precipitator Ash
5
Fly Ash and Flue Gas
6

FIGURE 3-1

INLET AND OUTLET STREAMS
AT STATION II

3.1 Coal

Five coal feeders (A, B, C, D, E) meter the coal from each of five storage silos to the respective mills for pulverizing prior to delivery to the boiler. Coal samples were collected every 15 minutes from one of feeders A, C, and E, consecutively, such that each of these three was sampled every 45 minutes. The samples were collected by passing a container of approximately 700 ml volume through the stream of coal falling from a conveyer in the feeder to the mill. The samples were combined in a large polyethylene container to form an integral sample for the entire period. This integral sample was riffled until two one-liter polyethylene bottles of representative sample remained for analysis.

3.2 Inlet Sluice Water

The sluice water was a cooling tower blowdown from a storage tank. Samples were collected from the storage tank by lowering a 250 ml polyethylene bottle through a portal in the top of the tank. Two 250 ml samples were collected every three hours from 8:30 AM to 5:30 PM during the primary sampling period on October 23rd and from 12:30 PM to 5:30 PM during preliminary sampling on October 22nd. The individual samples during each period were combined to form two integral samples which were acidified with nitric acid for preservation until analysis.

3.3 Sluice Solids

Samples of the ash sluice slurry stream were collected at the point of discharge into the ash pond during the pumping periods of both the preliminary and primary sampling. In reality the ash sluice stream was composed of three distinct streams: bottom ash sluice, economizer ash sluice, and pyrites from the coal mills. There were several variations in the mixing and order of pumping of each of the three streams. Bottom ash sluice was generally pumped separately, and economizer ash and pyrites were pumped both separately and combined. Due to the random nature of these combinations, a total ash sluice sample was the optimum method of obtaining a representative sample. Sluice pumping occurred at approximately four hour intervals on a 24 hour basis. The ash and pyrites accumulated during the preliminary sample period were sluiced from 4:22 PM to 5:51 PM on October 22nd. The ash and pyrites accumulated during the primary sample period were sluiced from 12:43 PM to 2:13 PM and from 4:10 PM to 5:31 PM on October 23rd. Samples were collected during each of these pumping intervals by passing a one-half liter polyethylene container vertically from top to bottom and bottom to top through the discharge stream every 2.5 minutes collecting a mixture of solids and liquid. The samples from each pumping interval were combined in a five gallon polyethylene container providing three integral samples. Upon arrival at our Austin laboratories, the solids and liquid in each sample were separated by filtration. The solids from the two samples collected during the primary sampling were combined to form an integral sample for analysis. The solids from the preliminary sample were retained as a reserve sample.

3.4 Outlet Sluice Water

The liquid portion of the ash sluice stream was sampled as described in Section 3.3. Following filtration two liters of the filtrate from the preliminary sample were acidified for preservation and retained as a reserve sample. The filtrates from the two primary samples were combined and a two liter portion of this integral sample was acidified for preservation and retained for analysis.

3.5 Precipitator Ash

Precipitator ash samples were collected from the ash storage silo through a portal in the top of the silo. Approximately one liter samples were collected hourly during the preliminary and primary sampling periods. The initial sample for each period was collected by dragging a polyethylene container, lowered through the portal by a rope, across the top of the ash in the silo until an adequate quantity was collected. The container was then left in the silo positioned such that the ash falling into the silo from the pneumatic conveyer system slowly filled the container over the period of an hour. The individual samples were combined to form an integral sample for each of the two sampling periods. These integral samples were riffled until two one-liter polyethylene containers remained of each. The two liters of ash from the primary sampling were retained for analysis and the two liters from the preliminary period were held as a reserve sample.

3.6 Fly Ash

Fly ash exiting the 500-foot stack in the flue gas stream at Station II was sampled through four four-inch sample ports. These were located on both ends of two perpendicular stack diameters at a height of 375 feet. A work platform was located at this level. The internal diameter of the stack was 25 feet at this point. The flue gas was at an average temperature of 324°F. The moisture content was determined by condensation during the sampling period to be 8.5%.

The sample ports were greater than ten stack diameters downstream from the point of entry of the flue gas and, therefore, a minimum of 12 traverse points, six on each diameter, were required to provide statistically valid sampling of the flue gas stream according to EPA Method 1. A total of 16 traverse points were sampled by dividing the cross-sectional area of the stack into four equal concentric areas and sampling at the centroid of each area along each of two perpendicular diameters. The sampling points were then the following distances from the inner stack wall:

1. 10 in.
2. 2 ft. 7 in.
3. 4 ft. 10 in.
4. 8 ft. 0 in.

The four inch pipe forming the sample port extended seven inches into the stack and was, therefore, so close to the first point that nonrepresentative turbulence was produced in the flue gas stream at the first point. In order to avoid the turbulence, the first sample point was moved an additional six inches into the stack.

Velocity measurements were taken at each point on October 21st and in conjunction with particulate loading determinations on October 22nd and 23rd as per EPA Method 2. The average velocity was found to be 61 fps with less than 10% variation over the three-day period. The velocity traverse results were used to determine the total flow in the stack and the conditions necessary for isokinetic sampling of the particulates. The velocity profile is shown schematically in Figure 3-2.

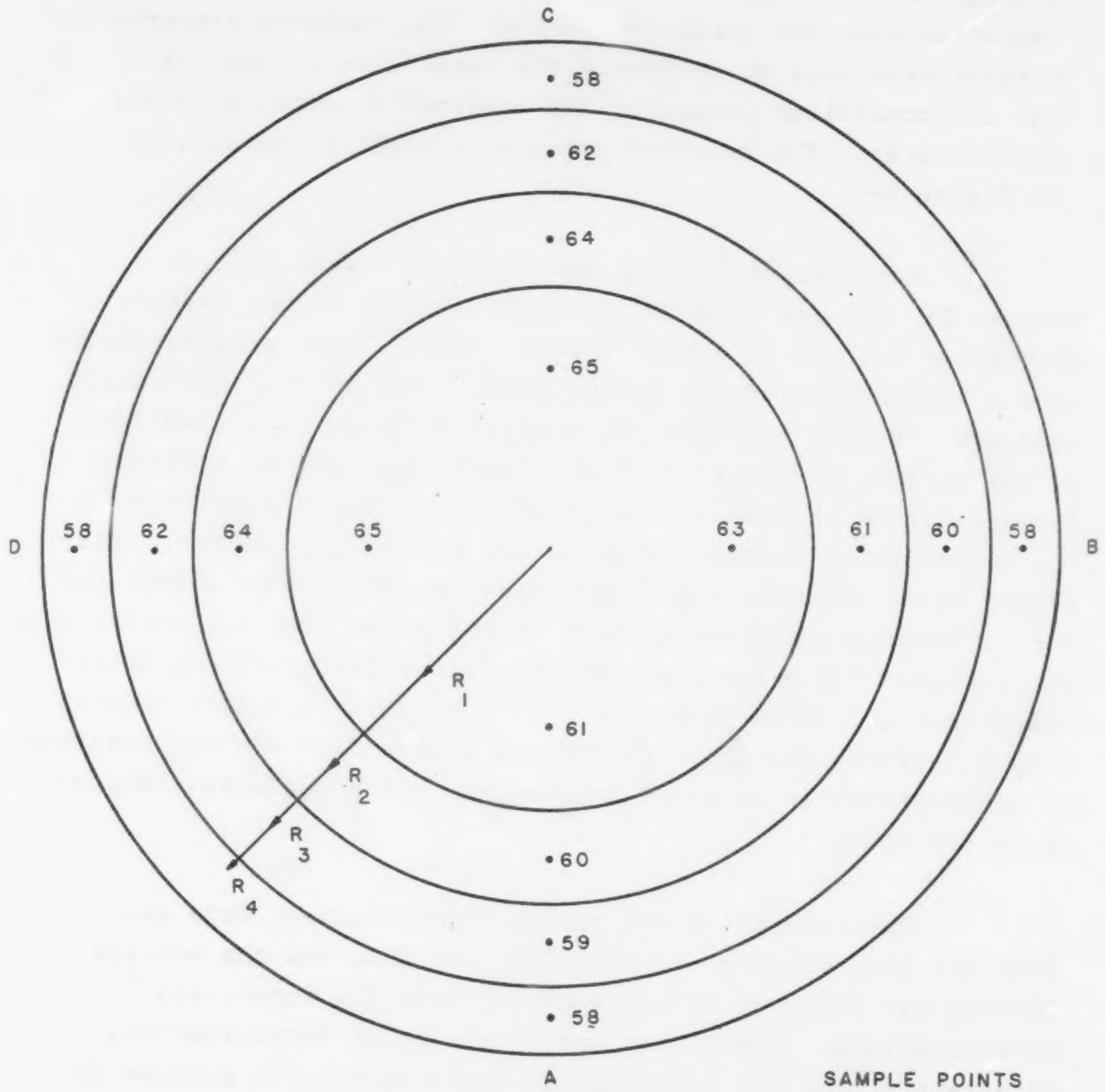
Particulate loading determinations were made on October 21, 22, and 23 with "in-stack" Gelman filter devices mounted at the end of a heat traced probe. These determinations were a combination of cumulative grain loadings and point grain loadings. During the cumulative grain loadings, the loadings at the individual points were physically averaged by sampling for equal time intervals at each point on a half diameter with the accumulation from all four points on a single filter. The single point grain loadings were taken at Point 4 to define the actual particulate concentration at the point used for particulate collection. The results of the cumulative grain loading determintations are shown in Figure 3-3. During particulate loading determinations, the moisture content of the flue gas was measured by condensation in an efficient copper tubing condenser maintained in an ice bath.

Particulate concentration determinations were made from all four ports on October 21st and 22nd and the average loading was found to be 0.018 gr/scf from the cumulative determinations. Cumulative and single point determinations were made during the particulate sample collection periods on October 22nd and 23rd from one sample port to detect any significant variations during sample collection.

FIGURE 3-2 - VELOCITY PROFILE AT STATION II

FOR OCTOBER 21, 1974

AVERAGE VELOCITY = 61 fps

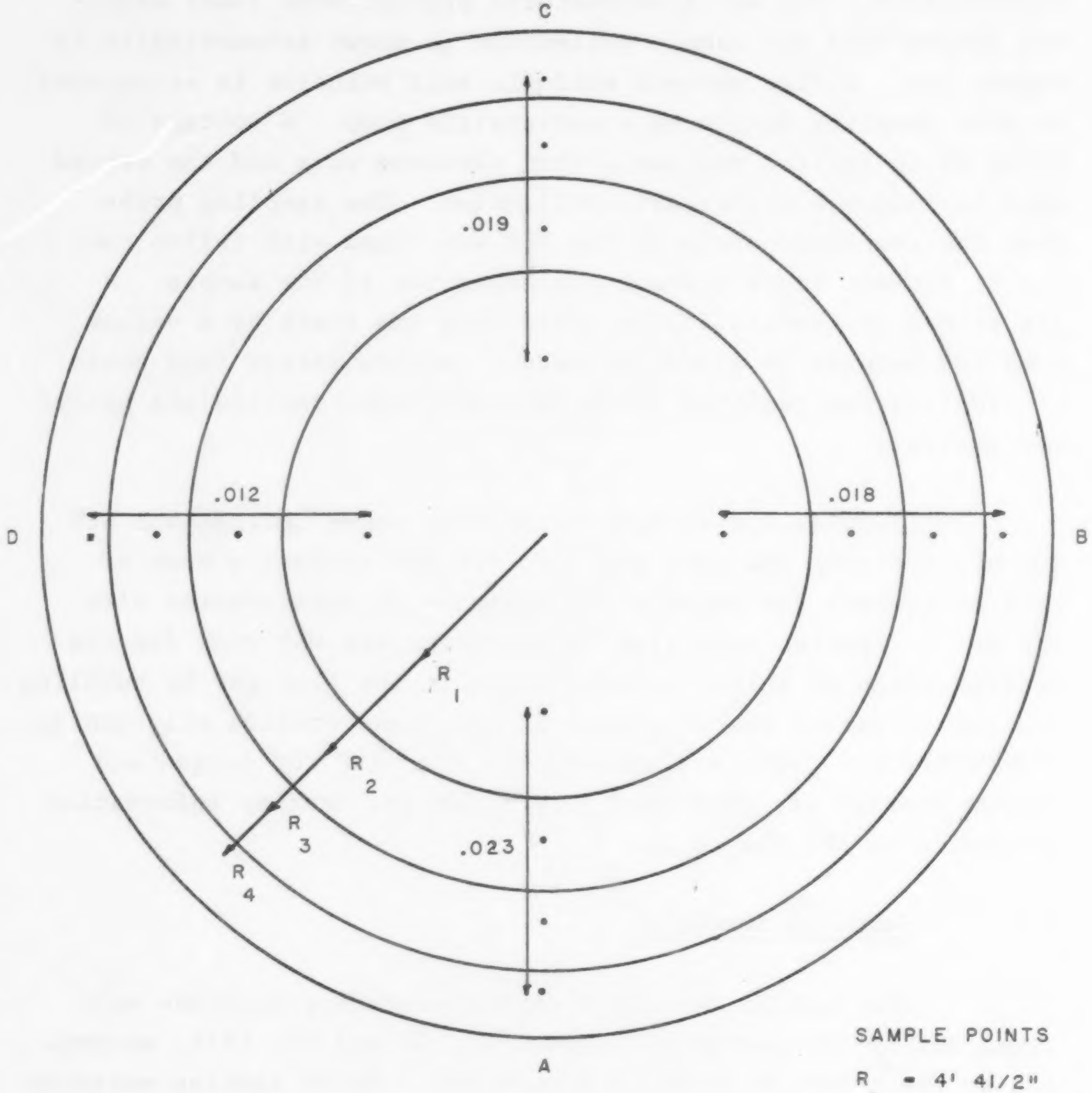

C
58
62
64
65
D
58
62
64
65
63
61
60
58
B
61
60
59
58
A
R_1
R_2
R_3
R_4

SAMPLE POINTS

R_1 = 4' 41/2"
R_2 = 7' 7"
R_3 = 9' 91/2"
R_4 = 11' 1/2"

FIGURE 3-3 - GRAIN LOADING AT STATION II

AVERAGE = 0.018 gr/scf


C
.019
D
.012
.018
B
R_1
R_2
R_3
R_4
.023
A

SAMPLE POINTS

R_1 = 4' 4 1/2"
R_2 = 7' 7"
R_3 = 9' 9 1/2"
R_4 = 11' 1/2"

Particulate matter in the flue gas stream was sampled at Point 4 on two perpendicular diameters during the preliminary sample period on October 22nd and the primary sample period on October 23rd. The wet electrostatic precipitator (WEP) sampling system used for sample collection is shown schematically in Figure 3-4. A five percent sulfuric acid solution is circulated in this sampling device by a peristaltic pump. A voltage of 12-14 KV is applied between a thin platinum wire and the wetted wall to induce electrostatic collection. The sampling probe from the sampling nozzle to the WEP was lined with teflon tubing to prevent trace element contamination of the sample. A gas stream is isokinetically drawn from the stack by a vacuum pump and metered by a dry gas meter. Approximately four hours of sampling was required to obtain sufficient particulate matter for analysis.

Samples for mercury vapor were taken during each WEP run by diverting the exit gas from the WEP through a mesh of gold wire where the mercury is collected by amalgamation with the gold. Samples were also taken during the WEP runs for the determination of sulfur concentration in the flue gas by bubbling a known volume of gas through a 3% hydrogen peroxide solution. by EPA Method 6. Orsat analysis of the flue gas for oxygen and carbon dioxide was performed to provide gas density information according to EPA Method 3.

3.7 Sampling Schedule

The samples described in the preceding sections were taken during the period of October 21, 22 and 23, 1974, according to the schedule shown in Figure 3-5. Those samples enclosed in parenthesis were analyzed, the rest being held in reserve.

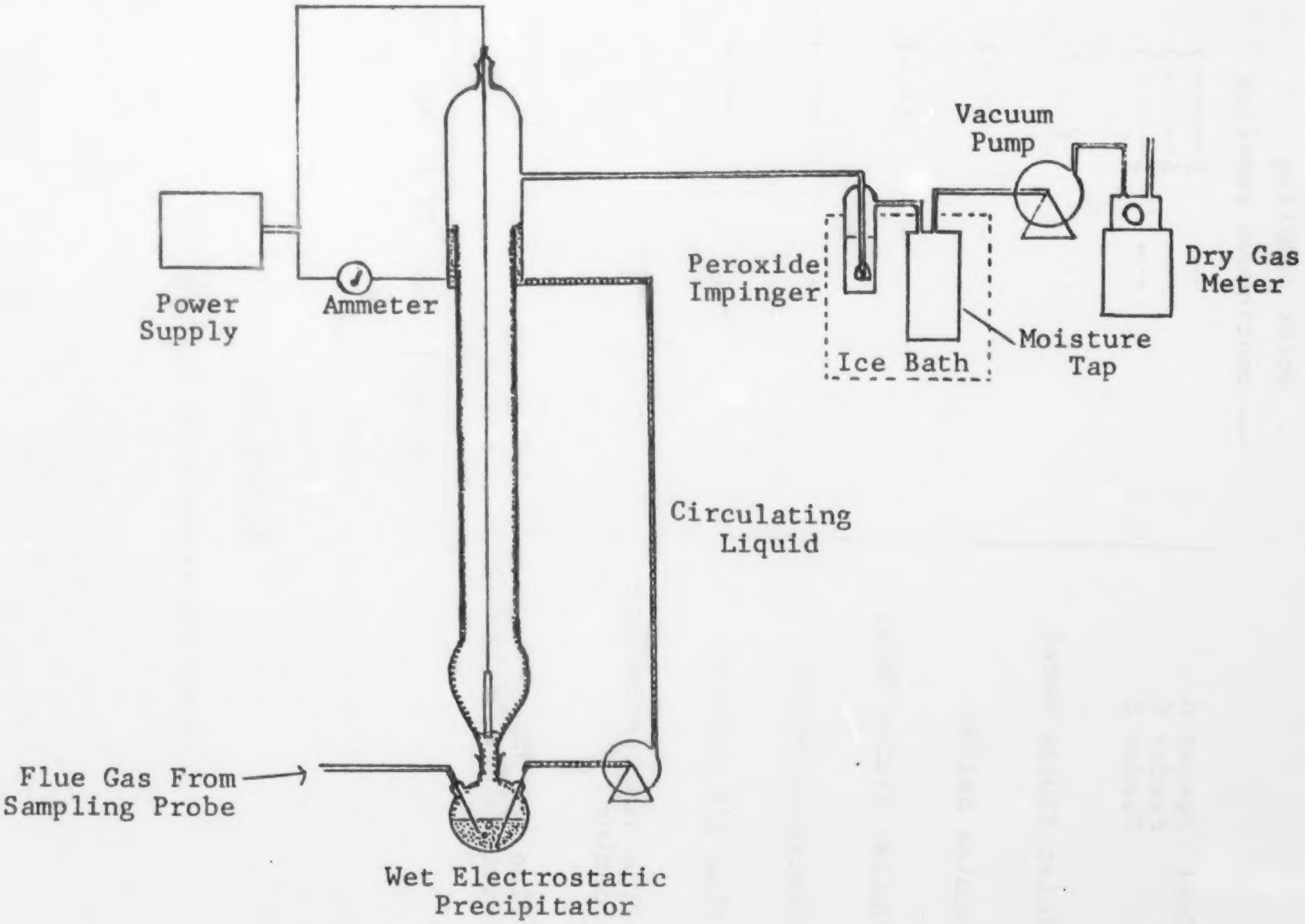

Vacuum Pump
Peroxide Impinger
Dry Gas Meter
Ice Bath
Moisture Tap
Power Supply
Ammeter
Circulating Liquid
Flue Gas From Sampling Probe
Wet Electrostatic Precipitator

FIGURE 3-4

SCHEMATIC OF STATION II
ARRANGEMENG FOR DUCT SAMPLING

. point sampling

— continuous sampling

	Oct. 21	Oct. 22	Oct. 23
1. Coal Feeder A		......	(..........)
Feeder C		......	(..........)
Feeder E		......	(..........)
2. Inlet Sluice Water		...	(....)
3. Sluice Solids		-	(- -)
4. Outlet Sluice Water		-	(- -)
5. Precipitator Ash		.....	(.........)
6. Flue Gas Velocity	—	— —	— —
7. Flue Gas Particulate Loading	-	— —	— —
8. Flue Gas WEP Particulate Collection		=	(= =)

FIGURE 3-5

Sampling Schedule at Station II

4.0 FLOW RATE MEASUREMENTS

The mass flow rate of each of the sampled streams described in Sections 3.0 to 3.6 was determined as described in the following sections.

4.1 Coal

The feed rate of coal to each of the mills is monitored by counters in the control room which record the revolutions of each of the five coal feeders. Each revolution of a feeder has been determined previously to be equivalent to 100 lb of coal. The readings of the five counters were recorded every hour during the sampling period and the total averaged over the period was found to be 3.88×10^5 lb/hr. From the moisture content of the coal of 29.2%, the dry coal flow rate was 2.75×10^5 lb/hr.

4.2 Inlet Sluice Water

The outlet pressure of the sluice pumps moving the sluice water from the sluice water storage tank to the economizer hopper, the bottom ash hopper and the pyrite storage area at the mills was recorded continuously during the pumping times for which samples were collected as described in Section 3.3. From an inlet head pressure of 10 psig and the pump curves supplied by the manufacturer, the inlet sluice water flow rate averaged over the two four-hour sluicing cycles on October 23rd was found to be 6.02×10^4 gph or 5.02×10^5 lb/hr.

4.3 Sluice Solids

The flow rate of the sluice solids was determined from an ash balance around the boiler and a split between sluice ash and precipitator ash of 22% sluice ash and 78% precipitator ash provided by plant personnel.

The average solids concentration in the sluice sample described in Section 3.3 was determined to be 1.48% by weight. Assuming this concentration to be representative of the sluice stream and a liquid flow rate in the stream (Section 4.2) of 5.02×10^5 lb/hr, the sluice solids flow rate was then 7.6×10^3 lb/hr by this method.

The coal burn rate was found to be 2.75×10^5 lb/hr on a dry weight basis (Section 4.1) and the ash content 7.23%. This predicts a total ash generation of 1.99×10^4 lb/hr. This ash is divided among precipitator ash, fly ash, economizer ash, bottom ash, and pyrites from the mill. The latter three comprise the sluice solids. Subtracting the fly ash rate of 1.40×10^2 lb/hr (Section 4.6) from the total and dividing the remainder between sluice ash and precipitator ash gives a sluice solids flow rate of 4.4×10^3 lb/hr. Assuming that the split between sluice ash and precipitator ash is between 17%-83% and 28%-73%, the error in the sluice solids flow is ±25%.

4.4 Outlet Sluice Water

The water losses in the sluicing system are negligible so the outlet sluice water flow rate is equal to the inlet sluice water flow rate of 5.02×10^5 lb/hr (Section 4.2).

4.5 Precipitator Ash

Similar to the sluice solids (Section 4.3), the precipitator ash mass flow rate was determined from an ash balance around the boiler.

The precipitator ash flow rate was determined from the difference between the total ash from the coal and the sum of the fly ash (Section 4.6) and the sluice solids (Section 4.3). This gives a precipitator ash production rate of 1.53×10^4 lb/hr ±10%.

4.6 Fly Ash

The flow rate of fly ash from the stack at Station II was determined from the flue gas velocity and particulate loading measurements discussed in Section 3.6. The total quantity of flue gas, corrected to standard conditions, is calculated from the average gas velocity in the stack and the cross-sectional area of the stack at the point of measurement. From the average velocity given in Section 3.6 of 61 fps and a cross-sectional area of 481 square feet, the total flow from the stack on a dry basis was 5.46×10^7 scfh. The fly ash emissions were then found from the total flow and an average particulate loading of 0.018 gr/scf to be 140 lb/hr.

4.7 Summary of Flow Rates

The mass flow of each of the streams sampled at the Station II are summarized in Table 4-1. The flow rates of all solids are based on dry weight.

TABLE 4-1

FLOW RATES FOR STREAMS
AROUND STATION II

Stream	Flow Rate
Coal	2.75×10^5 lb/hr
Inlet Sluice Water	5.02×10^5 lb/hr
Sluice Solids	4.4×10^3 lb/hr
Outlet Sluice Water	5.02×10^5 lb/hr
Precipitator Ash	1.53×10^4 lb/hr
Flue Gas	5.46×10^7 scfh
Fly Ash	1.40×10^2 lb/hr

APPENDIX B
ANALYTICAL PROCEDURES

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Trace element analyses on samples from three power plants were performed using dissolution and analytical techniques adapted specifically for these matrices.

1.0 SAMPLE PREPARATION

Preparation procedures were performed on the following types of samples to provide the primary digestion solution:

- Coal
- Coal Ash
- Sludge
- Lime
- Wet electrostatic precipitator
- Aqueous streams and filtrates

1.1 Coal, Coal Ash, and Sludge Preparation

The dissolution of coal, coal ash, and sludge is achieved by a two-step method. The samples are oxidized at 850-950°C in the presence of air utilizing a quartz pipe reactor. Volatile trace elements are retained via an acetone-dry ice trap at the end of the reactor. Dissolution of the remaining solids is accomplished by treatment with hydrofluoric, nitric, and sulfuric acid. The dissolved solids are then combined with the washings from the cold trap.

1.2 Lime/Limestone Preparation

Lime is dissolved by treatment with 5% hydrochloric acid. Any remaining undissolved material is removed by filtration and treated with hydrofluoric, nitric, and sulfuric acids to achieve dissolution.

1.3 WEP Preparation

An .8μ millipore filter was used to remove particulates from aqueous WEP samples. The particulates were then treated similar to coal (through the quartz pipe reactor acid dissolution steps). The filtrates, dissolved solids, and cold trap washings were quantitatively transferred to a single container to form the primary digestion sample.

1.4 Aqueous Streams and Filtrates Preparation

Nitric acid was added as a preservative to all aqueous samples.

2.0 ANALYTICAL PROCEDURES

The following analytical procedures were utilized for the determination of trace elements in the various samples. Each analytical technique has been screened for accuracy and reliability by standard addition and interference studies.

The complete analytical scheme for the analysis of trace elements in the samples are found in Figures 2-1, 2-2, 2-3, and 2-4. Detection limits for each procedure are summarized in Table 2-1.

2.1 Determination of Fluoride by the Ion-Selective Electrode Technique

The determination of fluoride utilizes a sodium carbonate fusion for solid samples (TH-060) and direct analysis of aqueous samples. The technique of standard addition using a fluoride specific-ion electrode, mentioned by several workers (BA-131, BA-137), is used for measurement of the fluoride ion. A citrate buffer is used to release complexed fluoride ions and to stabilize the pH and ionic strength. Addition of a standard quantity of fluoride is characterized by a change in the potential of the solution. The specific ion electrode senses this change in potential which is related to the initial fluoride concentration. The relationship between potential and fluoride concentration follows the Nernst equation:

$$\Delta E = A \log (C_F + X_i)/C_F$$

where,

ΔE is the change in potential

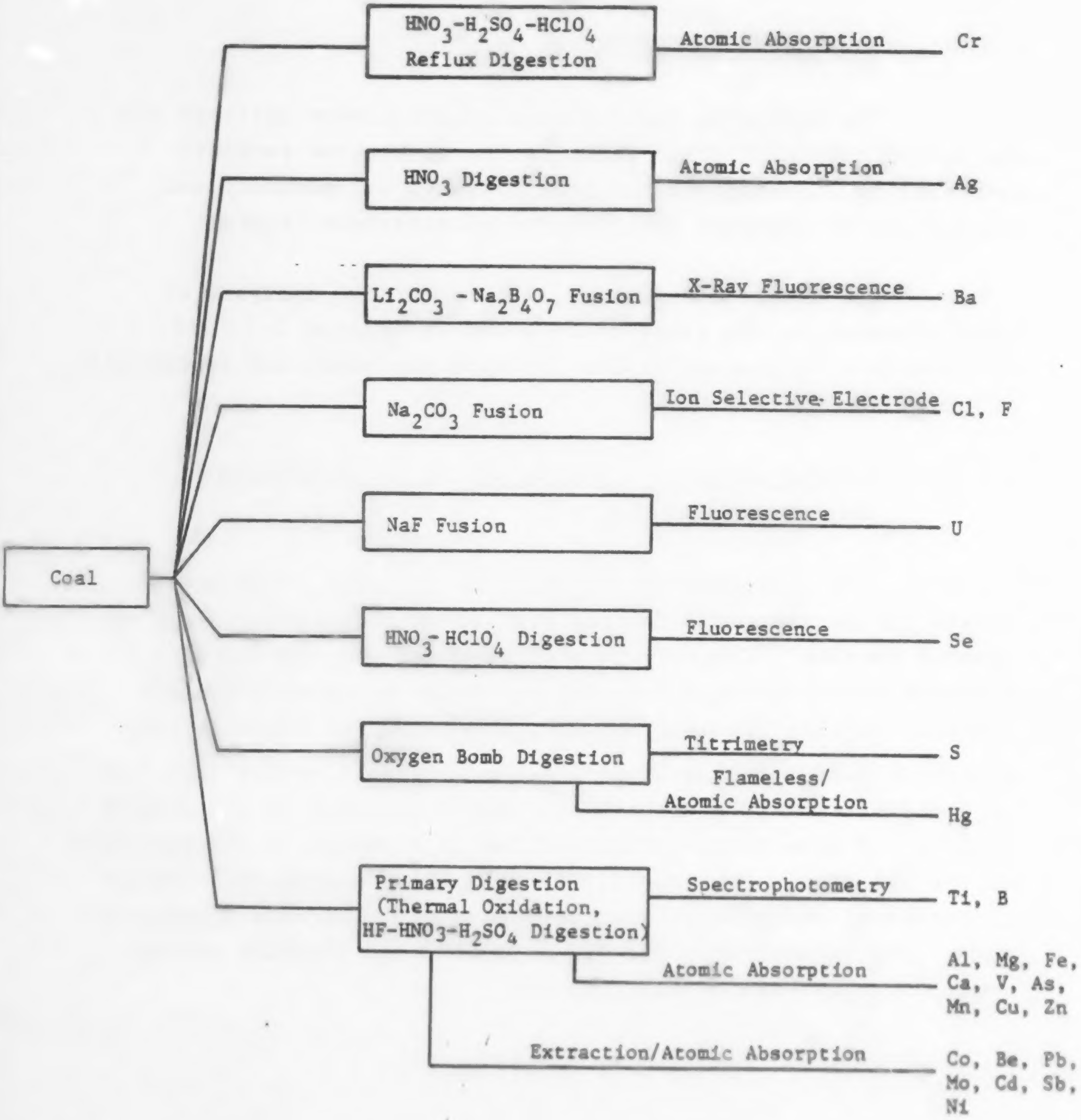
Coal
HNO_3-H_2SO_4-$HClO_4$ Reflux Digestion
Atomic Absorption
Cr
HNO_3 Digestion
Atomic Absorption
Ag
Li_2CO_3 - $Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
Na_2CO_3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO_3- $HClO_4$ Digestion
Fluorescence
Se
Oxygen Bomb Digestion
Titrimetry
S
Flameless/ Atomic Absorption
Hg
Primary Digestion (Thermal Oxidation, HF-HNO_3-H_2SO_4 Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni

FIGURE 2-1

ANALYSIS PROCEDURE FOR TRACE ELEMENT ANALYSIS
OF COAL

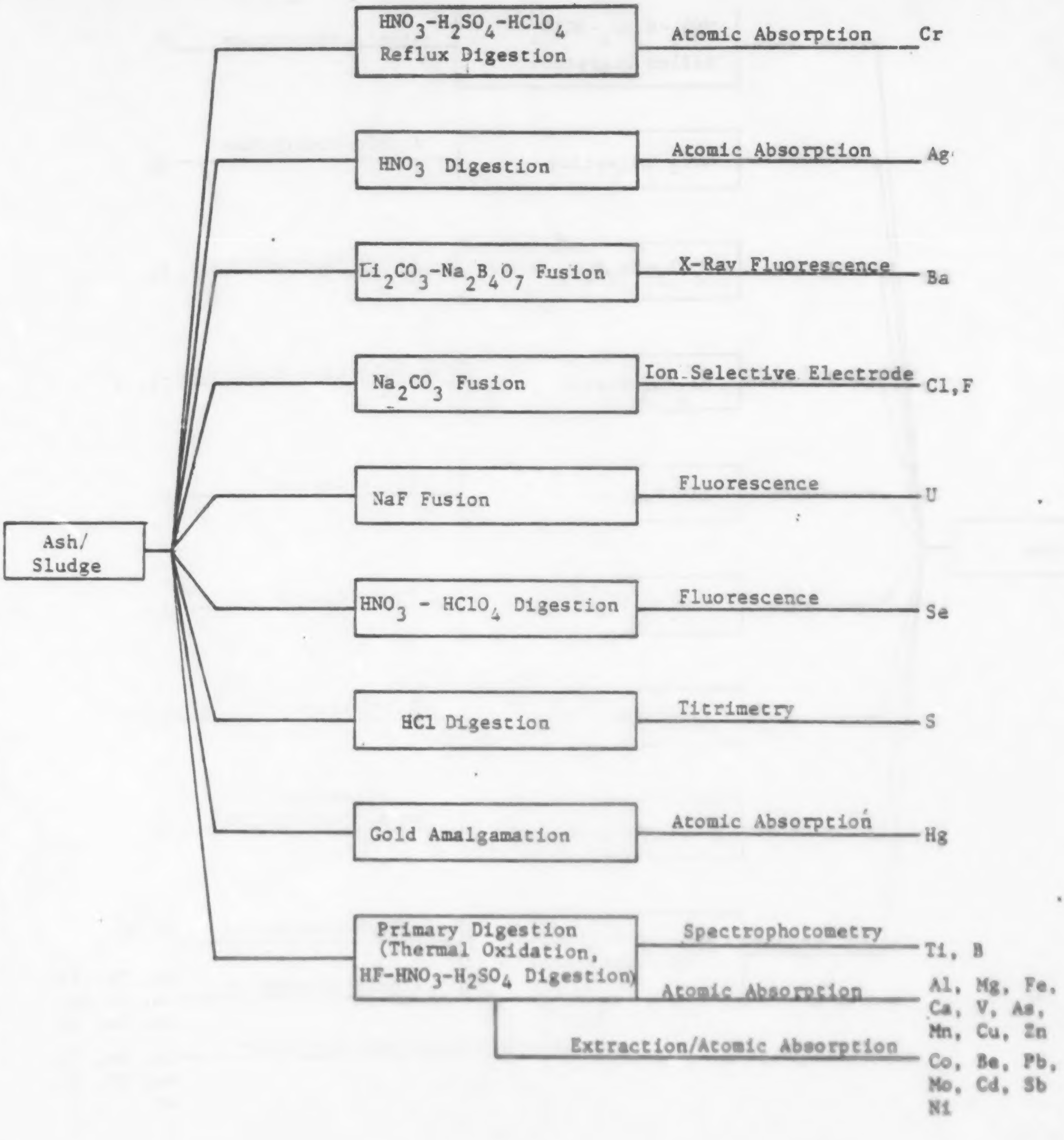
Ash/ Sludge
HNO3-H2SO4-HClO4 Reflux Digestion
Atomic Absorption
Cr
HNO3 Digestion
Atomic Absorption
Ag
Li2CO3-Na2B4O7 Fusion
X-Ray Fluorescence
Ba
Na2CO3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO3 - HClO4 Digestion
Fluorescence
Se
HCl Digestion
Titrimetry
S
Gold Amalgamation
Atomic Absorption
Hg
Primary Digestion (Thermal Oxidation, HF-HNO3-H2SO4 Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb Ni

FIGURE 2-2

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS
OF COAL ASH AND SLUDGE

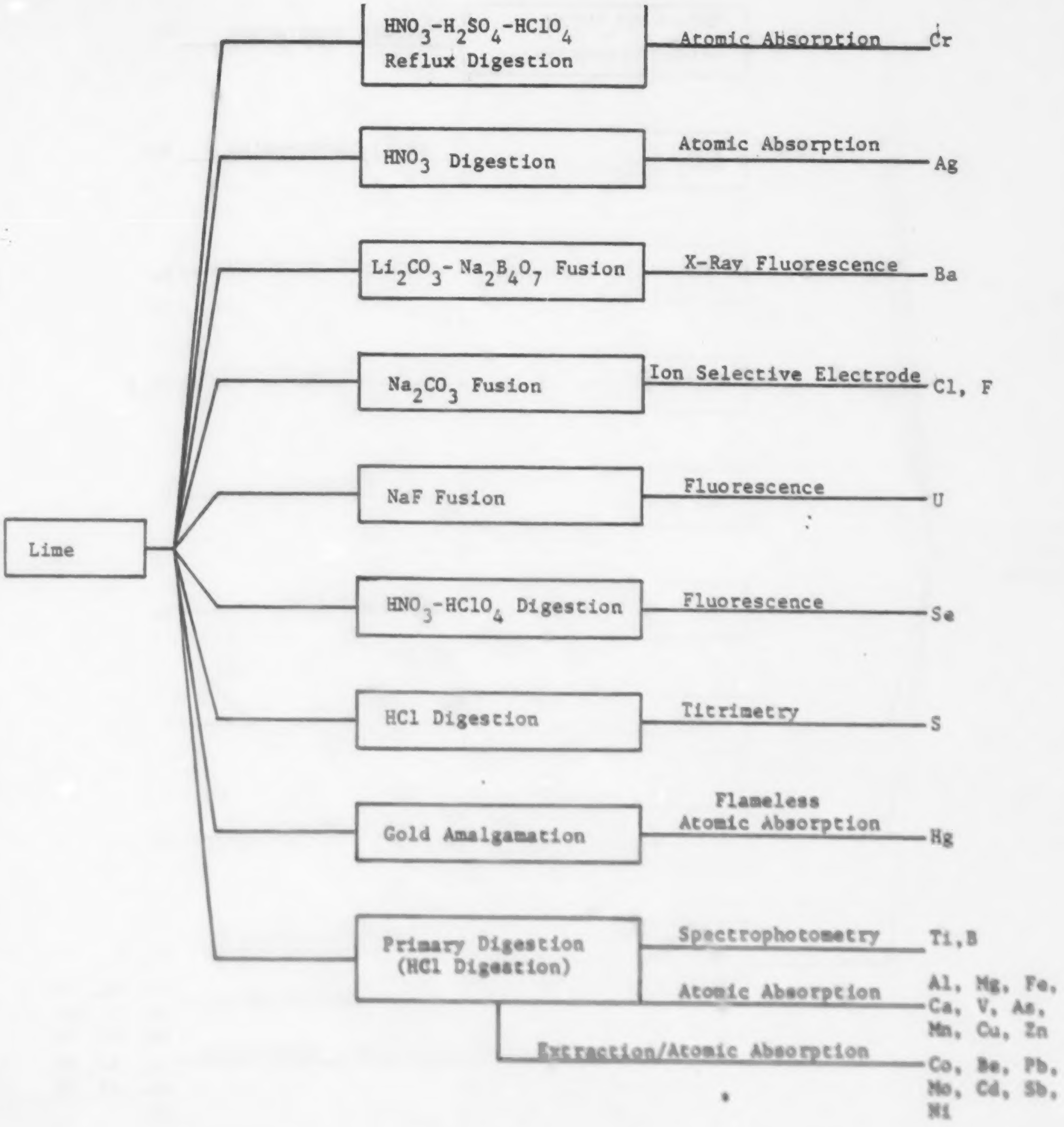
Lime
HNO3-H2SO4-HClO4 Reflux Digestion
Atomic Absorption
Cr
HNO3 Digestion
Atomic Absorption
Ag
Li2CO3- Na2B4O7 Fusion
X-Ray Fluorescence
Ba
Na2CO3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO3-HClO4 Digestion
Fluorescence
Se
HCl Digestion
Titrimetry
S
Gold Amalgamation
Flameless Atomic Absorption
Hg
Primary Digestion (HCl Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni

FIGURE 2-3

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS
OF LIME

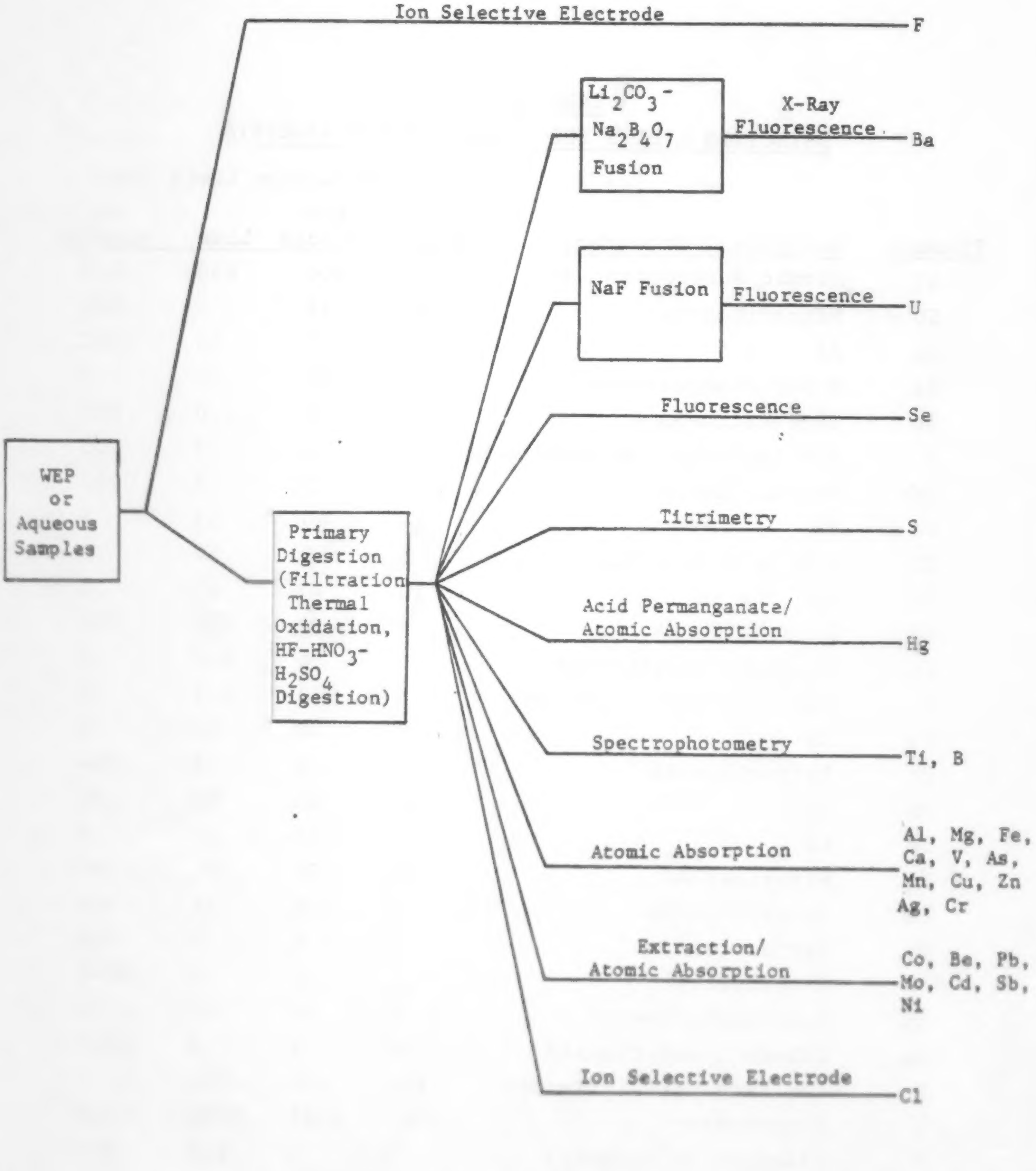
Ion Selective Electrode
F
Li_2CO_3-
$Na_2B_4O_7$
Fusion
X-Ray
Fluorescence
Ba
NaF Fusion
Fluorescence
U
Fluorescence
Se
WEP
or
Aqueous
Samples
Titrimetry
S
Primary
Digestion
(Filtration
Thermal
Oxidation,
$HF-HNO_3$-
H_2SO_4
Digestion)
Acid Permanganate/
Atomic Absorption
Hg
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe,
Ca, V, As,
Mn, Cu, Zn
Ag, Cr
Extraction/
Atomic Absorption
Co, Be, Pb,
Mo, Cd, Sb,
Ni
Ion Selective Electrode
Cl

FIGURE 2-4

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS
OF WET ELECTROSTATIC PRECIPITATOR LIQUORS AND AQUEOUS SAMPLES

TABLE 2-1

DETECTION LIMITS FOR TRACE ELEMENT ANALYSIS

Element	Analytical Procedure	Detection Limit (ppm) Coal	Ash Sludge	Lime	WEP Aqueous
Al	Atomic Adsorption (AA)	100	400	650	1.0
Sb	Extraction/AA	.04	.16	.6	.002
As	AA	.1	.5	.06	.001
Ba	X-Ray Fluorescence	5	50	40	.5
Be	Extraction/AA	.2	1.6	1.0	.001
B	Ion Exchange/Spectrophotometry	1	3	3	.05
Cd	Extraction/AA	.1	.2	.2	.0002
Ca	AA	10	40	65	.1
Cl	Ion Selective Electrode	5	10	10	.5
Cr	AA	10	40	65	.1
Co	Extraction/AA	.2	.8	1	.003
Cu	Standard Addition/AA	1	4	6.5	.1
F	Ion Selective Electrode	.5	1.2	1.2	.1
Fe	AA	10	40	65	.1
Pb	Extraction/AA	.4	.8	5	.004
Mn	AA	10	40	65	.01
Mg	AA	5	20	30	.5
Hg	Flameless AA	.01	.01	.01	.0005
Mo	Extraction/AA	.4	1.6	16	.004
Ni	Extraction/AA	2	8	2	.006
Se	Fluorometry	.1	.1	.1	.0005
Ti	Spectrophotometry	5	20	20	.1
Ag	Standard Addition/AA	.05	.2	.3	.0005
S	Ion Exchange/Titrimetry	100	100	200	5
U	Fluorometry	.0001	.0001	.0001	.0001
V	Standard Addition/AA	1	4	6.5	.005
Zu	Standard Addition/AA	1	4	6.5	.01

A is the constant = 59 mV at 25°C

C_F is concentration of free fluoride in solution

X_i is additional fluoride concentration added.

2.2 Determination of Chloride by Ion-Selective Electrode

Chloride is determined by a known standard addition method (OR-016). Sample preparation is the same as fluoride with a sodium carbonate fusion for all solid samples and direct analysis of aqueous solutions. A known amount of the species being measured is added to a known volume of sample and the resulting change in potential is observed. The original sample concentration is computed using a known addition table. The method allows samples to be analyzed which have variable ionic strength.

2.3 Spectrophotometric Determination of Titanium

Titanium is determined in the primary digestion solution as a yellow complex formed with tiron (disodium -1, 2- dihydroxybenzene -3, 5- disulfonate). This method is based on the procedure of Yoe and Armstrong, and is further extended to include shales by Rader (RA-125). An acetate buffer is used to regulate the pH. The only major interference is the complex tiron forms with Fe. This interference is eliminated by addition of sodium dithionite, reducing ferric to ferrous ion. The absorbance of the complex is read on a double beam spectrophotometer and samples compared with a standard calibration curve.

2.4 Determination of Copper and Zinc by Atomic Absorption

Copper and zinc are determined by direct aspiration of the primary digestion into the flame of the atomic absorption spectrophotometer (PE-115). Quantitative determinations are achieved by comparing the samples to their respective standards and by the use of standard additions to the primary digestions.

2.5 Determination of Molybdenum by Atomic Absorption

Molybdenum analysis is based on organic extraction atomic absorption technique and method of Joyner (JO-012) which has been modified by Kinrade and Van Loon (KI-085). Molybdenum in the primary digestion readily forms a complex with ammonium pyrrolidinedithiocarbamate at an acidic pH. Extraction of this complex with methyl isobutyl ketone offers a convenient method of concentration of the element. The signal is further enhanced by use of a nitrous oxide-acetylene flame. Concentration was determined by use of a standard calibration curve.

2.6 Determination of Nickel and Cobalt

Nickel and cobalt analyses are based on the organic extraction atomic absorption technique and method of Joyner (O-012). An ammonium tartrate buffer is used to stabilize the primary digestions. Nickel and cobalt are complexed with the chelating agent sodium diethyldithiocarbamate and extracted with methyl isobutyl ketone.

Once the metal complex has been separated and concentrated in the organic phase, the solution can be directly aspirated into atomic absorption spectrophotometer for measurement of the metal concentration.

2.7 Determination of Arsenic by Flameless Atomic Absorption

Arsenic is determined by a Radian modified flameless atomic absorption procedure based on the method of Ramakrishna, Robinson and West (RA-147) incorporation the techniques of Ediger (ED-027). The usually volatile arsenic present in the primary digestion is complexed as the molybdenum heteropoly acid with ammonium molybdate in a nitric acid medium. The complex formation enables the complex to be analyzed on the graphite furnace by reducing the volatility of the arsenic so that high temperature charring can be used to rid the sample of matrix interferences.

2.8 Determination of Antimony by Flameless Atomic Absorption

Antimony determination is based on a Radian flameless atomic absorption method modifying the extraction procedure of Burke (BU-136) and Headridge and Smith (HE-094) while utilizing the techniques of Ediger (ED-027) to reduce the volatility of antimony. After complexation with iodide, antimony is extracted from the primary digestion into a methyl isobutyl ketone and tributyl phosphate mixture (MIBK-TBP). TBP increases the extraction efficiency. As with arsenic, ammonium molybdate is used to increase the thermal stability of the complex during the charring cycle in the graphite furnace.

2.9 Determination of Beryllium by Atomic Absorption

The method of Bokowski (BO-027) is used for the determination of beryllium by atomic absorption. After addition of EDTA to the primary digestion to mask interferences, the beryllium present in the aqueous sample is chelated with acetylacetone. The complex is then extracted with methyl isobutyl ketone and the organic phase directly aspirated into the atomic

absorption spectrophotometer for the determination of beryllium. The solvent extraction procedure allows one to conveniently separate and concentrate the beryllium present.

2.10 Fluorometric Determination of Uranium

Radian's uranium procedure is a modification of the fluorometric determination of Thatcher (TH-049) updated by Turner (TU-025). Hexavalent uranium ions have a native fluorescence that may be used for analysis in relatively high concentrations. However, when fused with fluoride salts, uranyl ions produce an intense specific fluorescence detectable at levels of 10^{-10} grams of uranium. In general, the solid sample is mixed with a sodium fluoride flux and fused to a translucent disc in a platinum crucible. Aqueous primary digestions are evaporated in platinum crucibles and the residue fused with the flux. Once cooled, its fluorescence is measured with a Turner filter fluorometer. The method of standard additions is used to compensate for quenching.

2.11 Determination of Lead and Cadmium by Atomic Absorption

The procedure for analysis of lead and cadmium is similar to that for copper and zinc found in Section 2.4. Trace elements present in the primary digestion are separated and concentrated by chelation and extraction. Kinrade and Van Loon's method (KI-085) utilizing two chelating agents, ammonium pyrrolidinedithiocarbamate (APDC) and diethyl ammonium diethyldithiocarbamate (DDDC) to complex lead and cadmium has been highly successful. A citrate buffer was used due to its stability, strong buffering capacity, and nonparticipation in any reaction. The sample solution was extracted into methyl isobutyl ketone

and the organic solution injected into the graphite furnace on the atomic absorption spectrophotometer. Concentration was determined by use of a standard calibration curve.

2.12 Fluorometric Determination of Selenium

Selenium in the form of selinite reacts with aromatic orthodiamines to form piazselenols which fluoresce in various organic solvents. This method of determination of selenium is a Radian modification of a procedure published by Levesque and Vendette (LE-068). The solid sample is digested with nitric and perchloric acids in the Parr acid digestion bomb (MA-258). Aqueous samples are heated with nitric and perchloric acids. In both cases this oxidizes selenium to selenate and is followed by hydrochloric acid reduction to selinite. Isolation of selenite from interferring substances is accomplished by adding hydroxylamine, EDTA, and formic acid. The selenite is then reacted with 2, 3-diaminonaphthalene to form the organic extractable piazselenol, naphtho-(2, 3-d)-2 selena-1, 3-diazole, which is determined fluorometrically. This method is free of any interferences and is capable of detecting nanograms of selenium by use of a calibration curve.

2.13 Determination of Vanadium and Silver by Flameless Atomic Absorption

Vanadium is determined by flameless atomic absorption using the heated graphite atomizer. The method is a Radian adaptation of the work of Cioni, Innocente and Mazzioli (CI-002). Standard additions are performed on the primary digestion solution. Experimentation conducted on National Bureau of Standards samples of coal and coal ash yield results within 10% of the certified values.

Huffman (HU-095) recommends the same procedure for silver. Solid samples are dissolved in concentrated nitric acid and the method of standard additions is utilized.

2.14 Determination of Barium by X-ray Fluorescence

Barium is determined by a Radian method utilizing X-ray fluorescence. Samples are pelletized in a solid flux of lithium carbonate-sodium borate which are then introduced directly into the X-ray unit. Quantitative determinations are achieved by comparing the samples to a barium standard calibration curve prepared in the same manner and by the use of the method of standard additions to correct for matrix interferences, if any are present.

2.15 Determination of Chromium, Calcium, Iron, Magnesium, Manganese and Aluminum by Atomic Absorption

Chromium, calcium, iron, magnesium, manganese and aluminum (PE-115) are determined by direct aspiration into the flame of the atomic absorption spectrophotometer. Calcium and magnesium are diluted with lanthanum chloride to mase interferences. All elements are compared with standard calibration curves. All analyses are performed on the primary digestion solutions except chromium.

Chromium requires a special preparation for solid samples. Digestion of coal, ash, limestone, and sludge is accomplished with nitric, sulfuric, and perchloric acids in a reaction flash. A packed reflux column is attached to prevent any loss of chromium. Perchloric acid oxidizes all the chromium to Cr^{+6}. This method was developed by Rains and Menis (RA-155) as a mercury determination procedure. Radian has applied the method to the determination of chromium in NBS standard reference

materials of coal and coal ash and the results were comparable to the reported values.

2.16 Determination of Mercury by Flameless Atomic Absorption

Two methods were used for mercury analysis:

(1) acid permanganate

(2) gold amalgamation

Mercury is determined by a flameless atomic absorption technique. Liquid samples are treated with acid potassium permanganate to oxidize all of the mercury present to the +2 oxidation state. The excess $KMnO_4$ is removed with the addition of hydroxylamine hydrochloride, and the Hg^{+2} is reduced to elemental mercury by the addition of stannous chloride, which is swept through the absorption cell of the atomic absorption unit for determination.

Gold amalgamation collection of mercury has been reported by several workers (KA-086, DI-043). Radian utilizes a double amalgamation technique in which mercury is collected on a gold wire plug in a quartz tube either from flue gas passed through the tube or from thermal desorption into a stream of argon from solid samples. The mercury thus collected is desorbed by heating and amalgamated on a second tube to minimize interferences. Upon desorption from the second tube, the mercury is passed into an absorption cell positioned in the atomic absorption spectrophotometer.

2.17 Sulfur Determination by Titrimetry

The method of sulfur analysis consists of determining the total sulfur as sulfate by titrimetry. Initial sample preparation for coal is performed by ignition in a Parr Ignition Bomb and sorption of the evolved SO_2 in a sodium carbonate solution. Sludge and ash samples are mixed with hydrochloric acid and the solids filtered. In both cases, hydrogen peroxide is added to oxidize sulfite to sulfate. The sample is passed through a cation exchange column to form sulfuric acid. The acid is titrated with standard sodium hydroxide and the sulfur concentration determined.

Nitrate and phosphate ions interfere. Heat applied with hydrochloric acid at pH 2-4 avoids nitrite interference in the column. If the sample is heated at 275°C for 30 minutes to drive off sulfuric acid, phosphate can be determined and the value subtracted from the total to give sulfate ions.

2.18 Spectrophotometric Determination of Boron

Radian's boron procedure combines the separation method of Carlson (CA-084) and the spectrophotometric determination of Mair and Day (MA-190). An ion-exchange column is prepared using a boron specific resin, Amberlite XE-243, to separate boron in the primary digestion from interfering ions and allow complete boron recovery. It is then extracted into chloroform with 2-ethyl-1, 3-hexanediol. Boron in the organic phase is converted to the highly absorbing rosocyanin complex using glacial acetic acid followed by sulfuric acid. The absorbance of the complex is read on a double-beam spectrophotometer and samples compared with a standard calibration curve.

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COAL FIRED POWER PLANT
TRACE ELEMENT STUDY

VOLUME IV
STATION III

SEPTEMBER 1975

PREPARED FOR

ENVIRONMENTAL PROTECTION AGENCY
REGION VIII
DENVER, COLORADO

BY

RADIAN CORPORATION
AUSTIN, TEXAS

TS-1d

203

FOREWORD

The four volumes comprising this document describe a coal-fired power plant trace element study prepared under EPA Contract 68-01-2663.

This work was conducted under the direction of Mr. Terry L. Thoem, Project Officer, Environmental Protection Agency, Region VIII, Denver, Colorado. The Radian program staff included Dr. F. G. Mesich as Program Manager and Dr. K. Schwitzgebel as Technical Project Director. Principle contributors were Mr. R. A. Magee, Dr. F. B. Meserole and Mr. R. G. Oldham.

Acknowledgement is given to the station personnel from each utility company whose full cooperation greatly facilitated the field work. Mr. R. M. Mann, Mrs. G. E. Wilkin and Mrs. C. M. Thompson contributed significantly to the program during sampling and analysis.

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VOLUME IV

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APPENDIX A - SAMPLING AT STATION III

APPENDIX B - ANALYTICAL PROCEDURES

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TABLE OF CONVERSION UNITS

To Convert From	To	Multiply By
BTU	Calories, kg	0.25198
BTU/pound	Calories, kg/kilogram	0.55552
Cubic feet	Cubic meters	0.028317
Cubic yards	Cubic meters	0.76455
Feet	Meters	0.30480
Feet/second	Meters/second	0.30480
Gallons (U.S. liq.)	Cubic meters	0.0037854
Gallons (U.S. liq.)	Liters	3.7854
Gallons/minute	Cubic meters/minute	0.0037854
Grains/cubic foot	Grams/cubic meter	2.2884
Inches	Centimeters	2.5400
Inches of H_2O (4°C)	Millimeters Hg (0°C)	1.8683
Pounds	Kilograms	0.45359
Pounds/BTU	Kilograms/Calorie, kg	1.8001
Pounds/hour	Kilograms/hour	0.45359
Pounds/standard cubic foot (60°F, 29.92 inches Hg)	Kilograms/standard cubic meter (0°C, 760 mm Hg)	15.155
Tons	Metric tons	0.90719
Yards	Meters	0.9144

STATION III SUMMARY

The detailed sampling and characterization of trace elements in Station III streams resulted in excellent material balance closure for some 21 of the 27 elements examined in detail. A total of 53 elements were tested on a semiquantitative basis using spark source mass spectrometry.

A long-range objective is the correlation of the trace element content of each outlet stream with the coal input. A wide variation was found between elements as to their relative distribution in plant streams. The following elements were found to be concentrated in the flue gas stream.

Sulfur
Mercury
Chlorine
Antimony
Fluorine
Selenium
Lead
Molybdenum
Nickel
Boron
Zinc
Cadmium
Chromium
Copper
Cobalt

In contrast, the following elements are more or less distributed in direct proportion to the total ash content of each stream.

Barium
Beryllium
Vanadium
Aluminum
Calcium
Iron
Manganese
Magnesium
Titanium

The elements uranium, arsenic, and silver display intermediate behavior.

These characteristics of a lignite-fired cyclone boiler with mechanical ash collection are compared with other plant configurations and coal compositions in Volume I of this report series.

1.0 INTRODUCTION

The use of the extensive coal resources in the Northern Great Plains area of the United States may provide a significant part of the country's energy growth for the foreseeable future. As natural gas and oil resources become less available and more costly, coal will receive increasing emphasis as a primary energy source. A coal-fired generating station produces a variety of emissions and effluents ranging from sulfur and nitrogen oxides and particulates in the flue gas to solid and liquid wastes.

In addition to carbonaceous material, coal contains inorganic matter which becomes part of the emissions and effluents from the generating station. The overall objective of this program was to define the sources, levels, and disposition of potentially toxic trace and minor elements in power plant streams. The levels of trace elements in various streams may be expected to be a function of both coal composition and plant operating configuration.

This volume describes the detailed characterization, with respect to trace and minor elements, of a lignite-fired, cyclonic boiler using mechanical collection of particulate matter. The particular plant designated as Station III operates at a design rating of 250 MW.

The following trace elements were examined in detail:

Aluminum
Antimony
Arsenic
Barium
Beryllium
Boron
Cadmium
Calcium
Chlorine
Chromium
Cobalt
Copper
Fluorine
Iron
Lead
Manganese
Magnesium
Mercury
Molybdenum
Nickel
Selenium
Silver
Sulfur
Titanium
Uranium
Vanadium
Zinc

A material balance was calculated for each element to provide a sound basis for evaluating the reliability of the emissions measurements. In addition, each sample was surveyed using spark source mass spectrometry to provide a semi-quantitative assessment of 53 trace elements.

The following sections give a description of the plant, a discussion of the sampling, analytical strategies, and presentation and discussion of the experimental data. Appendices are provided which describe the sampling of the plant and the analytical methodology.

2.0 SAMPLING AND SAMPLE HANDLING

The procedures used to sample Station III are presented briefly in this section. Details are given in depth in Appendix A, "Sampling at Station III". Sampling was performed during the period 26-30 August 1974.

2.1 Plant Description

Station III is a 250 MW unit firing North Dakota lignite. The lignite is mined in a nearby strip mine operation, trucked to the plant, crushed and fed to the coal-storage silos. The boiler arrangement is of the cyclonic type. Bottom ash and economizer ash are sluiced intermittently to a nearby pond. Cyclones are used as fly ash control devices. The station is a base load unit. Fluctuation in plant load ranged from 245-250 MW during the entire sampling period.

2.2 Sampling Points and Flow Rate Determinations

The streams sampled are shown schematically in Figure 2-1. The incoming streams are coal and ash sluice water taken from the cooling pond. Outgoing streams are bottom ash, bottom ash sluice water, economizer ash, economizer sluice water, cyclone ash and flue gas containing fly ash. The physical location of the points for sampling these streams at the station are schematically shown in Figure 2-2.

Sample Point 1: Coal

The coal is stored in seven silos. A coal sample was collected from silos number 2, 4, and 6 each 20 minutes

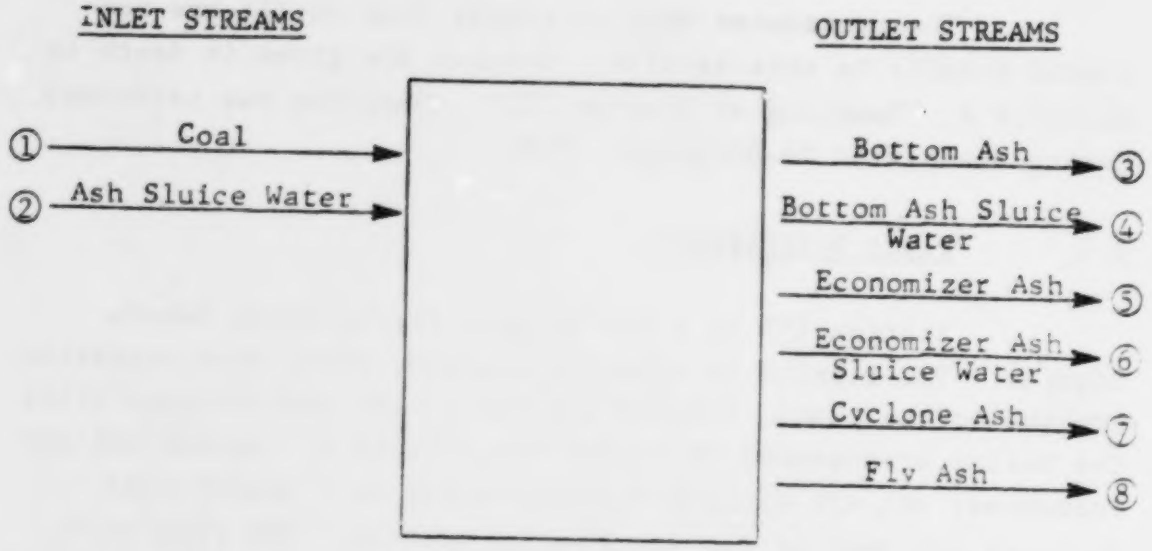
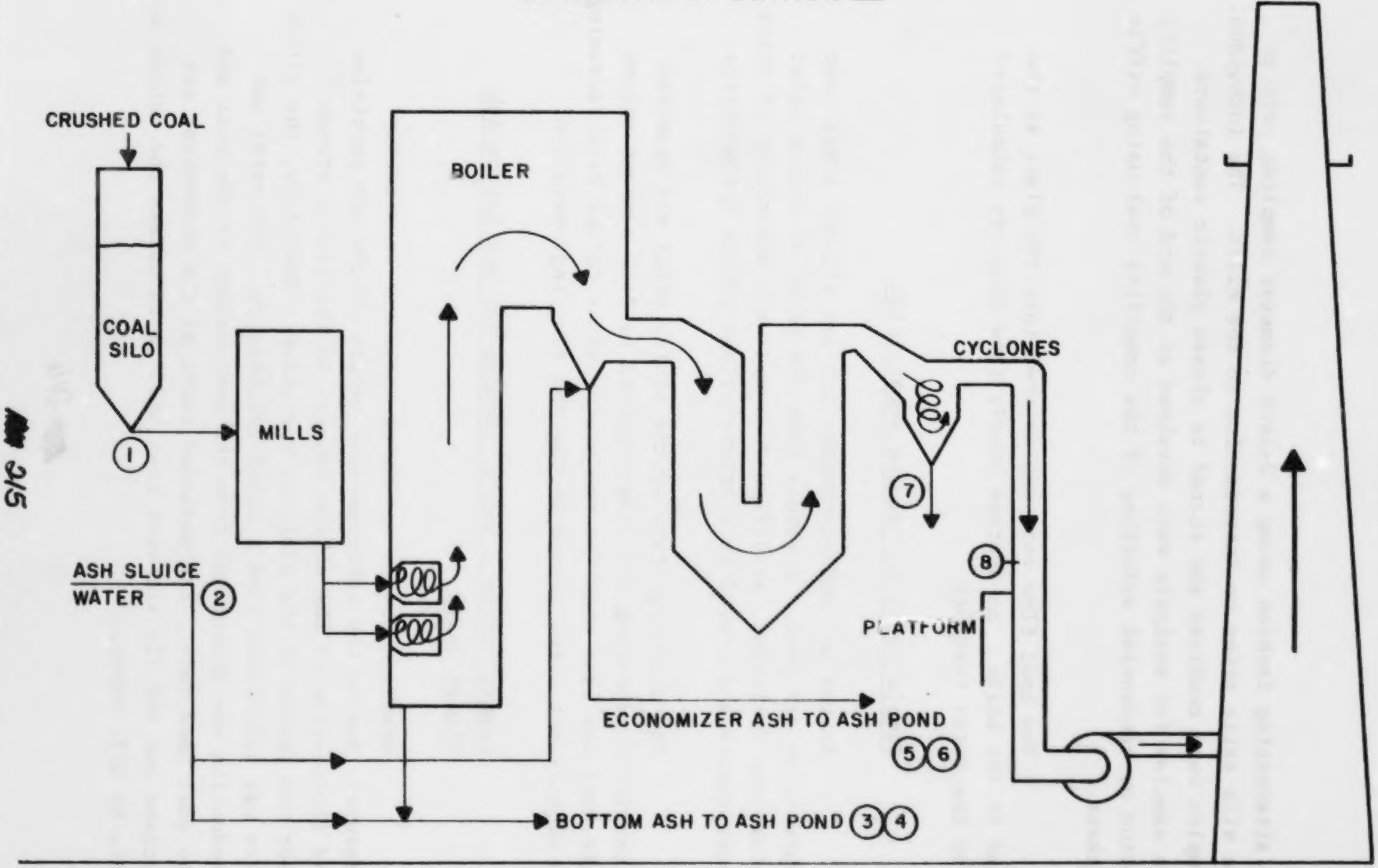

INLET STREAMS
OUTLET STREAMS
① Coal
② Ash Sluice Water
Bottom Ash ③
Bottom Ash Sluice Water ④
Economizer Ash ⑤
Economizer Ash Sluice Water ⑥
Cyclone Ash ⑦
Fly Ash ⑧

FIGURE 2-1

Inlet and Outlet Streams

at Station III

FIGURE 2-2
SCHEMATIC OF STATION III


CRUSHED COAL
COAL SILO
①
MILLS
BOILER
ASH SLUICE WATER
②
CYCLONES
⑦
⑧
PLATFORM
ECONOMIZER ASH TO ASH POND
⑤⑥
BOTTOM ASH TO ASH POND ③④

in alternating fashion using a 2-inch diameter sampling port at the silo exits prior to introduction to the mills. The individual samples were combined and stored in closed plastic containers. Two samples for analysis were obtained at the end of the sampling period by sequential splitting of the composite coal using riffle buckets.

The coal flow rate was metered into the plant at the feed to the mills. An average hourly flow rate was calculated from the meter readings.

Sample Point 2: Sluice Water Inlet

Bottom ash and economizer ash are sluiced every four hours to an ash pond. A sample from the point of sluice water intake was collected, acidified to avoid wall adsorption of trace constituents and stored in a polypropylene bottle for analysis.

The discharge rate of the sluice water was measured directly by measuring the time required to fill a known volume. This rate was also used for the sluice water intake rate, assuming no significant water losses during the sluicing operation.

Sample Points 3 and 4: Bottom Ash and Bottom Ash Sluice Water

Accurate bottom ash rates could not be directly measured, due to the inhomogeneous nature of the ash particles and fluctuation of the solids content in the sluice stream over the period of the sluicing operation. Therefore, the solids rate was calculated from a total ash balance. The total ash production was determined from the ash content of the coal and the coal feed rate. The measured rates of the economizer ash, cyclone ash and fly ash were then used to calculate the bottom ash rate by difference.

The liquid sluice water exit rate was determined by measuring the time necessary to collect a known volume of the total sluice stream.

Sample Points 5 and 6: Economizer Ash and Economizer Sluice Water

Samples of this stream were collected at the sluice outlet. The total flow rate of solids and liquids was determined by timed volumetric collection of the total stream. Individual discharge rates for economizer ash and economizer sluice water were calculated from this value using the solids content of the slurry input. The slurry in this case was sufficiently uniform to permit determination of both solids and liquid flow rates.

The liquid samples were stored in polypropylene bottles and acidified after filtration. The solid portions were divided and two samples retained for analysis.

Sample Point 7: Cyclone Ash

The cyclone ash was collected from the pneumatic system used to transport the ash to the cyclone ash storage silo. The pneumatic transport system was shut down each hour, the sight glasses removed and samples taken from the hoppers of Cyclones 1, 4 and 7. Two integral samples were obtained by riffling at the end of the sampling period. The cyclone ash flow rate was calculated from the ash disposal truck weights, moisture content, density and the difference in the storage silo levels determined during the sampling period.

Sample Point 8: Flue Gas and Fly Ash

The flue gas and fly ash are discharged from the cyclones to the stack through two ducts, differentiated as north and south ducts in this report. Each duct was equipped with four sampling ports.

The velocity profile was determined using S-type pitot tube and thermocouple measurements as per EPA Method 2. Individual values obtained in the center of 16 equal-sized rectangles according to EPA Method 1 were then averaged to determine an integral value for the south and the north ducts.

The dust loadings were measured at the same set of points. Gelman filter devices were used to determine dust loadings in each of the section squares for both ducts. Average grain loadings for the north and south ducts were then calculated from the individual flows found in the 16 rectangles.

Particulate matter for analysis was collected with wet electrostatic precipitators (WEP). This method of collection permits sampling over an extended time at isokinetic conditions without plugging, as occurs in a filter. Thus, a sufficient quantity of sample can be collected to permit repeated analyses. In addition, problems of trace element contamination by the filter substrate are avoided. A detailed description of the WEP device is given in Appendix A. To confirm the comparability of this sampling approach with the filter technique recommended by EPA, an EPA filter was run in series with the WEP. A 125 mm Gelman class "A" glass filter was used in a glass filter holder which was placed in the sampling train immediately after the WEP. The whole assembly was heated to avoid condensation of sulfur acid mist. The particulate matter collected by the filter during four WEP runs was equivalent to a grain loading of 0.0009 grains/scf. The inlet particulate loading to the WEP was 0.21 grains/scf, giving a collection efficiency of the WEP of 99+%.

The WEP samples were collected at a single point in the duct and a correction made from the grain loading at this point to the average grain loading. The dust concentration at the sampling point was determined from the calcium and titanium concentrations in the WEP sample assuming that these elements are evenly distributed in the particulates with respect to particle size. This assumption is based on work performed by Davison, et al. (DA-105) in which fly ash samples were collected from the duct of a coal-fired station. Andersen impactor samplers were used to separate the particulates into seven size fractions. The results of this work for calcium and titanium are presented in Table 2-1. It is evident from these data that the assumption of uniform ash composition with respect to calcium and titanium holds within experimental limits.

The relationship between particle size and titanium and calcium concentration in the fly ash is important to this correction because the cyclone ash has a larger average particle size than the exiting fly ash. If the titanium concentration were dependent on particle size then the assumption made in Equation (2-1) that the titanium and calcium concentration in the fly ash is the same as in the cyclone ash is invalid.

The point grain loadings were determined from the calcium and titanium concentrations in the WEP samples and the calcium and titanium weight fractions found in the cyclone ash using the relation:

$$\text{Point grain load (gr/scf)} = \frac{15.4\ V_L}{2\ V_G}\left[\frac{XW_L(\mathrm{Ca})}{XW_{Ash}(\mathrm{Ca})} + \frac{XW_L(\mathrm{Ti})}{XW_{Ash}(\mathrm{Ti})}\right] \qquad (2\text{-}1)$$

TABLE 2-1
CALCIUM AND TITANIUM ANALYSES* OF ANDERSEN IMPACTOR PARTICLE SIZE FRACTIONS (DA-105)

Particle Diameter µm	Ca wt%	Ti wt%
>11.3	4.9	1.12
7.3 - 11.3	-	-
4.7 - 7.3	4.2	0.92
3.3 - 4.7	-	-
2.06 - 3.3	5.0	1.59
1.06 - 2.06	-	-
0.65 - 1.06	2.6	1.08

* Analysis by X-ray fluorescence spectrometry

where,

V_L = volume of the WEP liquor (ml)

V_G = volume of flue gas sampled by WEP (scf)

$XW_L(\mathrm{Ca})$ = concentration of calcium in WEP liquor (μg/ml)

$XW_{Ash}(\mathrm{Ca})$ = weight fraction of calcium in the cyclone ash (ppm)

$XW_L(\mathrm{Ti})$ = concentration of titanium in WEP liquor (μg/ml)

$XW_{Ash}(\mathrm{Ti})$ = weight fraction of titanium in the cyclone ash (ppm)

The point to average grain loading correction factor is then the ratio of the average grain load in each duct to the point grain load calculated from equation (2-1). The correction factors were 1.7 for the south duct and 2.4 for the north duct. These factors not only compensate for spatial maldistribution of the particulates but also for temporal variation since the WEP samples are taken over a longer period of time than the grain loading determinations.

Gaseous mercury in the flue gas was collected by gold amalgamation. Hydrogen peroxide bubblers were used to absorb SO_2 in the flue gas by EPA Method 6.

2.3 Summary of Flow Rates and Estimated Errors

A summary of the flow rates is given in Table 2-2. The error limits presented in this table are largely based on

TABLE 2-2
FLOW RATES FOR STREAMS
AROUND STATION III

Stream	Flow Rate	Error Limit	Method Used For Flow Determination
Coal	2.34×10^5 lb/hr.	±10%	Revolutions of coal feeders were measured
Bottom ash and economizer ash sluice water inlet	2.65×10^5 lb/hr.	±15%	Rates were set equal to sluice water outlet rates
Bottom ash	1.68×10^4 lb/hr.	±15%	Difference of ash rate in incoming coal and discharge rates of economizer ash, cyclone ash and fly ash
Bottom ash sluice water outlet	1.78×10^5 lb/hr.	±15%	Directly measured by volume
Economizer ash	154 lb/hr.	±20%	Calculated from economizer ash sluice rate
Economizer ash sluice water outlet	8.71×10^4 lb/hr.	±15%	Directly measured by volume
Cyclone ash	6.23×10^3 lb/hr.	±10%	Measured by weighing trucks and from differences in silo level
Flue gas	4.11×10^7 scfh	±10%	Measured by duct traverses
Fly ash	3.42×10^3 lb/hr.	±10%	Determined from point grade loadings

Radian field experience and the typical errors expected with the flow measuring devices. Also summarized in this table are the procedures used to obtain the listed rates.

2.4 Sampling Schedule

With the exception of the bottom ash and economizer ash, all plant streams were continuous with short residence times in the system. Bottom ash accumulated in the quench tanks and was sluiced to the storage basin every four hours requiring approximately thirty minutes to empty the tank. Economizer ash accumulated in the economizer ash hopper for four hours after which the accumulation was then sluiced to the storage basin over a period of approximately thirty minutes. Sampling of these two streams was time-phased to collect samples from the sluice stream representative of the ash which had accumulated during the sampling period.

Sampling was performed during the period August 27-29th according to the schedule shown in Figure 2-3. Those samples enclosed in parenthesis were analyzed, the rest were retained in reserve.

2.5 Sample Analysis

The techniques used for the quantitative determinations were based on:

(1) atomic absorption
(2) X-ray fluorescence
(3) ion selective electrodes
(4) fluorometry, and
(5) colorimetry.

. point sampling
— continuous sampling

	August 27	August 28	August 29
1. Coal - Silo 2			(........)
Silo 4			(........)
Silo 6			(........)
2. Bottom Ash and Economizer Ash Sluice Water Inlet		•	(•)
3. Bottom Ash		•	•(•)
4. Bottom Ash Sluice Water Outlet		•	•(•)
5. Economizer Ash		•	•(•)
6. Economizer Ash Sluice Water Outlet		•	•(•)
7. Cyclone Ash		•	(........)
8. Flue Gas Velocity	—	—	—
9. Flue Gas Particulate Loading		—	—
10. Flue Gas WEP Particulate Collection		=	(==)

FIGURE 2-3
Sampling Schedule at Station III

The methods are described in greater detail in Appendix B, "Analytical Procedures".

Figures 2-4 through 2-6 give a succinct survey of dissolution and analytical methods used for trace element determination in the samples.

The analytical accuracies of the employed techniques are summarized in Table 2-3. These values were derived by comparing analytical results with NBS standards where available. In the other cases, recovery studies and/or precision values are the basis for the estimated confidence level.

Semiquantitative analyses based on spark source mass spectrometry (SSMS) for 53 elements were performed by Accu-Labs, Inc. Since the accuracy of this method is strongly dependent on the matrix, an error limit could not be estimated in the framework of the present study.

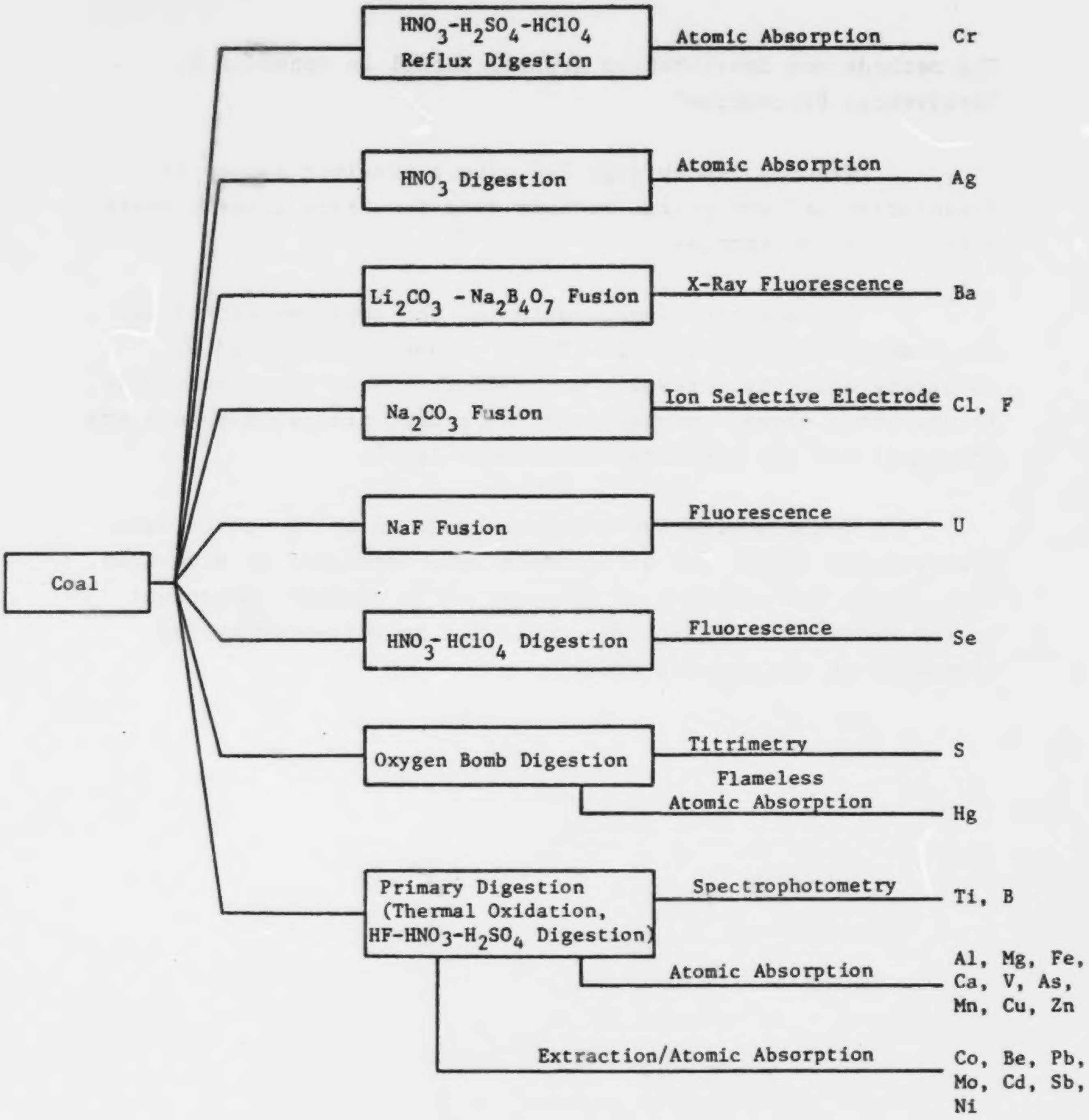

Coal
$HNO_3-H_2SO_4-HClO_4$ Reflux Digestion
Atomic Absorption
Cr
HNO_3 Digestion
Atomic Absorption
Ag
$Li_2CO_3 - Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
Na_2CO_3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
$HNO_3 - HClO_4$ Digestion
Fluorescence
Se
Oxygen Bomb Digestion
Titrimetry
S
Flameless Atomic Absorption
Hg
Primary Digestion (Thermal Oxidation, $HF-HNO_3-H_2SO_4$ Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni

FIGURE 2-1

ANALYSIS PROCEDURE FOR TRACE ELEMENT ANALYSIS
OF COAL

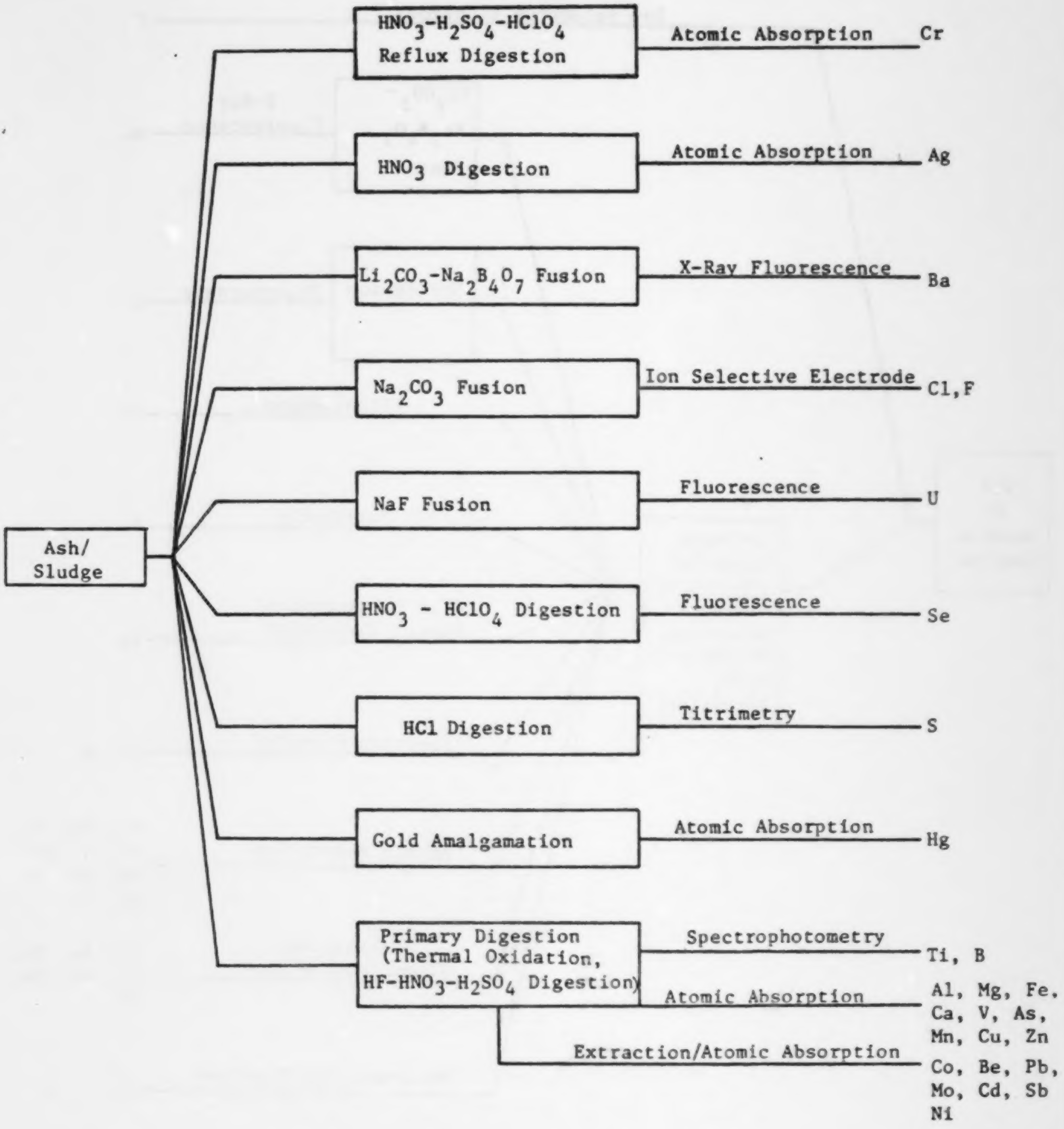

Ash/ Sludge
$HNO_3-H_2SO_4-HClO_4$ Reflux Digestion
Atomic Absorption
Cr
HNO_3 Digestion
Atomic Absorption
Ag
$Li_2CO_3-Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
Na_2CO_3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO_3 - $HClO_4$ Digestion
Fluorescence
Se
HCl Digestion
Titrimetry
S
Gold Amalgamation
Atomic Absorption
Hg
Primary Digestion (Thermal Oxidation, $HF-HNO_3-H_2SO_4$ Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe. Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb Ni

FIGURE 2-2

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS OF COAL ASH AND SLUDGE

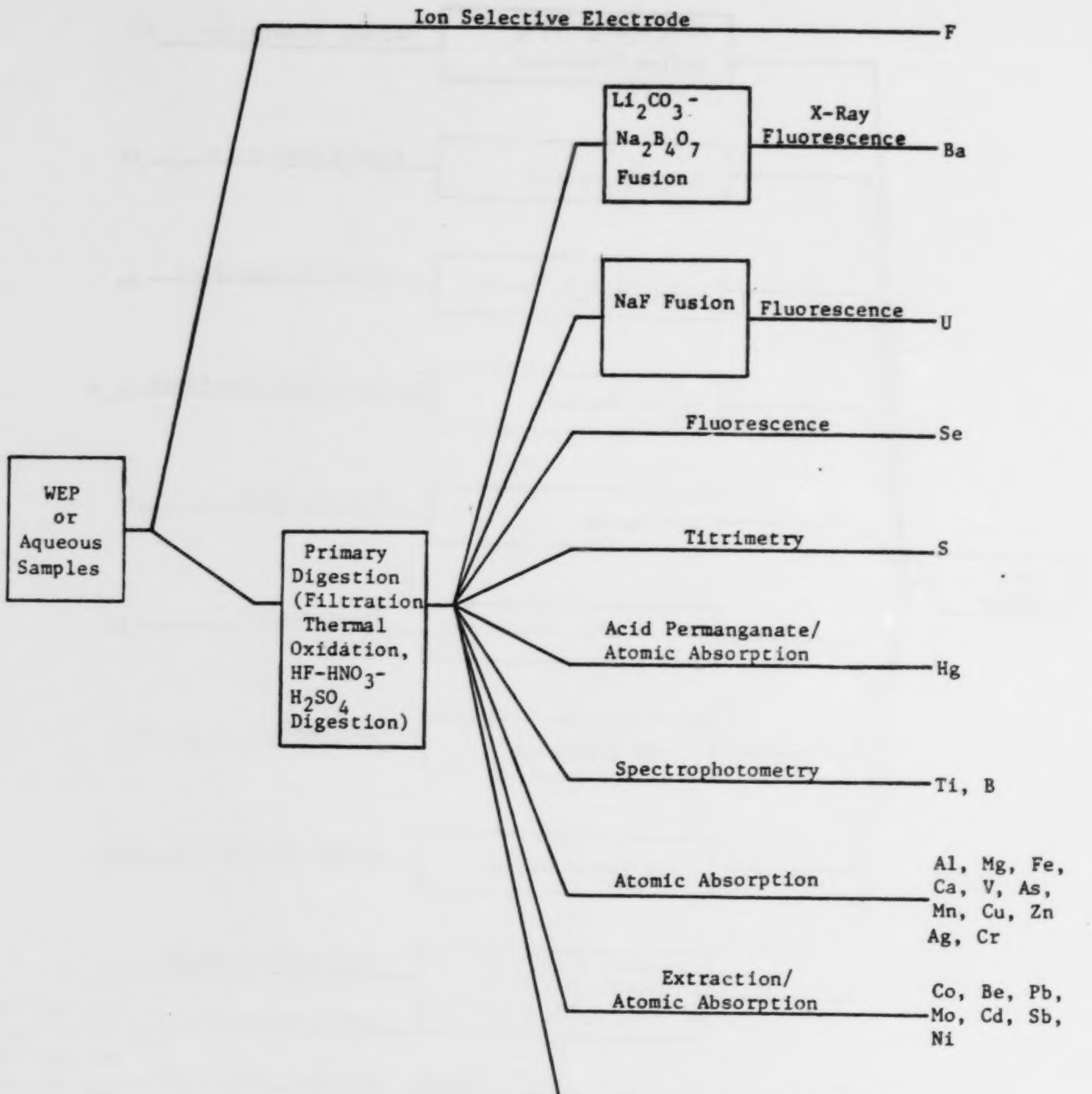

Ion Selective Electrode
F
Li_2CO_3-
$Na_2B_4O_7$
Fusion
X-Ray
Fluorescence
Ba
NaF Fusion
Fluorescence
U
Fluorescence
Se
WEP
or
Aqueous
Samples
Titrimetry
S
Primary
Digestion
(Filtration
Thermal
Oxidation,
$HF-HNO_3$-
H_2SO_4
Digestion)
Acid Permanganate/
Atomic Absorption
Hg
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe,
Ca, V, As,
Mn, Cu, Zn
Ag, Cr
Extraction/
Atomic Absorption
Co, Be, Pb,
Mo, Cd, Sb,
Ni
Ion Selective Electrode
Cl

FIGURE 2-4

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS
OF WET ELECTROSTATIC PRECIPITATOR LIQUORS AND AQUEOUS SAMPLES

TABLE 2-3

ESTIMATED ERROR LIMITS FOR THE CHEMICAL ANALYSES

	WEP Liquor	Aqueous Samples	Coal and Coal Ash
Aluminum	±10	±10	± 8
Antimony	±10	±10	±15
Arsenic*	± 8	± 8	±10
Barium	±20	±20	±20
Beryllium	±10	±10	±12
Boron	± 8	± 8	± 8
Cadmium*	±12	±12	±12
Calcium	± 2	± 2	± 2
Chlorine	±10	±10	± 8
Chromium*	±10	±10	±12
Cobalt	±10	±12	±10
Copper*	±10	±10	±12
Fluorine	± 8	± 8	± 8
Iron*	± 6	± 6	± 6
Lead*	±10	±10	±18
Manganese*	±10	±10	± 8
Magnesium	± 2	± 2	± 2
Mercury*	±20	±10	±10
Molybdenum	±12	±12	±15
Nickel*	±12	±12	±12
Selenium*	± 5	± 5	± 5
Titanium	± 8	± 8	± 8
Silver	±10	±10	±10
Sulfur	±10	± 2	± 2
Uranium*	± 8	± 8	± 6
Vanadium*	±12	±12	±10
Zinc*	±10	±10	±12

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*By comparison with NBS Standard Reference Materials 1633 and 1634.

3.0 DATA EVALUATION

The flow rates and chemical analyses are used to calculate the transport rate of the elements of interest through the boiler and their discharge rates in the effluent streams. A material balance is made around the boiler for each of the elements. The mathematical correlation forms are given in the next sections.

3.1 Trace Element Material Balances

The transport rates of the elements of interest through the steam station are calculated from the chemical analyses of the samples and the flow rates of the incoming and exiting streams. A material balance is calculated for each of the trace elements to verify the determined emission values.

Equating the trace element flow into the system to the flow out of the system gives the following expression:

$$M_c \cdot XW_c(j) + M_{asw} \cdot XW_{asw}(j) = \qquad (3\text{-}1)$$

$$M_{ba} \cdot XW_{ba}(j) + M_{basw} \cdot XW_{basw}(j) + M_{ea} \cdot XW_{ea}(j) + M_{easw} \cdot XW_{easw}(j) + M_{ca} \cdot XW_{ca}(j) + V_{fgs} \cdot XV_{fgs}(j) + V_{fgn} \cdot XV_{fgn}(j)$$

where

M_c = the mass flow rate of coal into the boiler on a dry weight basis (lb/hr.)

$XW_c(j)$ = the weight fraction of the element j in the coal on a dry weight basis

M_{asw} = the mass flow rate of the inlet sluice water to the ash sluice system (lb/hr.)

$XW_{asw}(j)$ = the weight fraction of the element j in the inlet sluice water

M_{ba} = the discharge rate of bottom ash from the boiler (lb/hr.)

$XW_{ba}(j)$ = the weight fraction of the element j in the bottom ash

M_{basw} = the mass flow rate of the sluice water discharged with the bottom ash (lb/hr.)

$XW_{basw}(j)$ = the weight fraction of the element j in the bottom ash sluice water

M_{ea} = the discharge rate of economizer ash from the boiler (lb/hr.)

$XW_{ea}(j)$ = the weight fraction of element j in the economizer ash

M_{easw} = the mass flow rate of the sluice water discharged with the economizer ash (lb/hr.)

$XW_{easw}(j)$ = the weight fraction of the element j in the economizer ash sluice water

M_{ca} = the discharge rate of ash collected in the cyclone dust collectors (lb/hr.)

$XW_{ca}(j)$ = the weight fraction of element j in the cyclone ash

V_{fgs} = the volumetric flue gas flow rate in the south duct (scfh)

$XV_{fgs}(j)$ = the weight of the element j per unit volume of flue gas in the south duct (lb/scf)

V_{fgn} = the volumetric flue gas flow rate in the north duct (scfh)

$XV_{fgn}(j)$ = the weight of element j per unit volume of flue gas in the north duct (lb/scf)

3.2 Error Propagation Analysis

An error propagation analysis was performed on the material balance equations for each element. Error limits are calculated for the total inlet and outlet rates of each element indicating the magnitude of variation to be expected due simply to random errors.

Only errors random in nature are considered in this treatment. A variance is calculated for a given value according to the following standard definition.

$$S^2(Q) = \sum_{i}^{n} \left(\frac{\partial Q}{\partial q_i}\right)^2 S^2(q_i) \qquad (3\text{-}3)$$

where

$S(Q)$ = the variance in Q

Q = the material balance value which is a function of the q_i's

q_i = the $i^{\underline{th}}$ independent flow rate or composition used to calculate Q

Confidence intervals can then be assigned to the trace element flow rates calculated for the various streams based on the errors associated with each measurement used in the calculation of these quantities. These limits will be included with the calculated rates discussed in the following section. The error limits for the flow rates were given in Table 2-2 and those assigned to the chemical analyses were listed in Table 2-3.

4.0 RESULTS

The values for the proximate and ultimate analysis of the coal are presented in Table 4-1, the coal ash analysis in Table 4-2.

The analysis results using the quantitative analytical methods described in Section 2.5 and Appendix B are listed in Table 4-3. The element concentrations in the coal and the flow rates are reported on a dry weight basis. Most of the values in Table 4-3 are presented in parts per million on a dry weight basis for the solid samples or micrograms per milliliter for liquids. Some elements present in higher concentrations are listed as percent. The WEP results are presented in pounds per standard cubic foot of dry flue gas, where standard conditions are defined as a temperature of 60°F and pressure of 29.92 inches of mercury.

Table 4-4 presents the analytical results obtained by SSMS. The coal sample was analyzed in duplicate to estimate the precision of this method of analysis. The duplicate results differ in some cases by a factor up to three as indicated for Br, Cd, Ce, Cu, Ni, Rb, and Zn. Systematic errors caused by special matrices could not be determined within the scope of the present work. Blind duplicate samples were also submitted for the WEP samples from the south duct. The differences between duplicate samples were fairly large as evidenced by a factor of 8 for Br, 5 for Cd, 22 for Cs, 20 for Cr, etc. However, these data (SSMS) are useful for order-of-magnitude estimates of trace element flows.

The trace element flow rates in lb/hr are listed in Table 4-5, using the quantitative analysis methods and in Table 4-6, using the SSMS results. The sum of the elemental flow rates

TABLE 4-1
STATION III COAL ANALYSIS
Radian Sample No. 496

Proximate		As Received	Dry
% Moisture		36.84	0.00
% Ash		7.84	12.40
% Volatile Matter		26.24	41.54
% Fixed Carbon		29.08	46.06
	Total	100.00	100.00
% Sulfur		0.91	1.44
BTU/lb		6214	9838
Moisture and Ash Free BTU/lb	11,230		

Ultimate			
% Carbon		41.91	66.52
% Hydrogen		6.77	4.24
% Nitrogen		0.60	0.95
% Oxygen		41.97	14.59
% Sulfur		0.91	1.30
% Ash		7.84	12.40
	Total	100.00	100.00

TABLE 4-2

STATION III ASH ANALYSIS

Radian Sample No. 496

Mineral Analysis of Ash	Percent
Silicon Dioxide, SiO_2	30.21
Aluminum Oxide, Al_2O_3	11.90
Titanium Dioxide, TiO_2	0.67
Iron Oxide, Fe_2O_3	14.27
Sodium Oxide, Na_2O	3.24
Potassium Oxide, K_2O	1.10
Calcium Oxide, CaO	16.23
Magnesium Oxide, MgO	5.72
Phosphorus Pentoxide, P_2O_5	0.09
Sulfur Trioxide, SO_3	12.90
Other	3.67
Total	100.00

Ash Viscosity Calculations	
Basic Content (percent)	48.66
Acidic Content (percent)	51.34
Dolomite Content (percent)	54.13
Base-to-Acid Ratio	0.95
Silica-to-Alumina Ratio	2.54
Temperature for 250 Poise Viscosity, ^{o}F	2050

TABLE 4-3

ANALYTICAL RESULTS OF THE STATION III SAMPLES[1]

Element	Coal	Ash Sluice Water Inlet	Bottom Ash	Bottom Ash Water Sluice	Economizer Ash	Economizer Ash Sluice Water	Cyclone Ash	South Duct WEP	North Duct WEP
Aluminum	.74%	.42	8.79%	1.7	8.48%	.58	7.44%	730	440
Antimony	.40	.018	.8	.034	.56	.021	.79	.18	.13
Arsenic	8.0	.006	20.	.0087	126.	.0012	188.	.67	1.3
Barium	440.	<.5	.57%	<.5	.83%	<.5	.77%	<5.8	<5.3
Beryllium	.60	.0014	5.3	.0017	8.8	.003	8.3	.027	.021
Boron	150.	.26	520.	.25	740.	2.4	.16%	.71	.34
Cadmium	.20	.0003	.87	.0011	1.8	.0012	2.9	.054	.059
Calcium	1.38%	35.	13.0%	43.	12.0%	46.	13.1%	1800	1100
Chlorine	55.	12.	88.	16.	119.	17.	135.	29	43
Chromium	13.	< .053	95.	<.053	121	< .053	86.	3.5	3.6
Cobalt	.75	.0003	10.	.0041	12.	.0039	13.	.28	.21
Copper	10.5	.0084	50.	.014	94.	.008	145.	1.9	1.6
Fluorine	57.	.21	< 10.	.25	65.	.21	670.	29	33
Iron	.75%	.43	6.54%	2.1	6.69%	1.4	5.76%	930	550
Lead	.86	.015	< .8	.024	8.3	.025	8.2	.26	.33
Magnesium	.37%	26.	3.71%	26.	3.77%	24.	3.63%	7.1	4.3
Manganese	79.	.082	720.	.055	900.	.096	750.	450	260
Mercury	.074	< .0005	< .010	< .0005	.12	< .0005	.17	.080	.086
Molybdenum	2.0	.033	18.	.016	44.	.012	61.	2.1	3.7
Nickel	5.4	.006	23.	.0014	36.	.007	38.	2.3	3.0
Selenium	1.3	.0012	.25	.0011	.14	.0012	9.5	.31	.26
Titanium	350.	<.1	.35%	<.1	.38%	<.1	.30%	15	18
Silver	.034	<.0003	.11	<.0003	.32	<.0003	.75	<.0031	<.0032
Sulfur	1.44%	68.	95.	74.	.13%	77.	.87%	7000	7400
Uranium	1.5	.0022	3.2	.0035	11.	.0044	12.	.15	.086
Vanadium	15.	<.005	140.	<.005	110.	<.005	86.	2.5	2.2
Zinc	7.8	.013	18.	.013	140.	.028	120.	3.5	2.2

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[1] Values represent the average of duplicate determinations. Values for liquid samples are reported as ug/ml and solids samples as ppm on a dry basis, unless otherwise noted. WEP values are reported as 10^{-8} lb/scf (60°F, 29.92" Hg).

TABLE 4-4: STATION III, ANALYTICAL RESULTS BY SS-MS[1]

Elements	Coal[2]		Inlet Ash Sluice Water	Bottom Ash	Bottom Ash Sluice Water	Economizer Ash	Economizer Ash Sluice Water	Cyclone Ash	South Duct WEP[2]		North Duct WEP
Aluminum	2200	~1200	1.2	>1%	0.74	>1%	1.2	>1%	163	390	43
Antimony	0.47	0.35	--	2.5	0.003	2.5	--	2.5	0.13	0.34	0.075
Arsenic	9.4	6.0	0.005	12	0.012	57	0.020	120	1.1	2.6	0.59
Barium	260	490	0.31	730	0.40	~2600	0.31	~1800	8.8	0.49	2.3
Beryllium	2.1	3.2	--	56	--	11	--	11	0.012	<0.012	0.011
Bismuth	<0.77	<0.85	--	<0.17	--	0.35	--	1.5	0.023	0.058	0.011
Boron	250	250	<0.1[4]	~1000	<0.1	~2000	<0.1[4]	~2500	[5]	[5]	22
Bromine	1.9	4.4	0.025	3.1	0.070	3.1	0.012	5.5	0.023	0.19	0.022
Cadmium	1.4	3.4	0.029	1.3	0.37	2.9	0.029	1.3	1.6	10.	1.0
Calcium	>1%	>1%	33	>1%	41	>1%	47	>1%	1000	1000	75
Cerium	7.5	17	0.005	40	0.002	71	0.001	71	0.31	0.19	0.19
Cesium	0.16	0.33	0.001	0.43	0.006	1.1	0.001	4.3	0.26	0.012	0.34
Chlorine	110	110	0.19[3]	26	2.0[3]	92	0.37[3]	52	0.42	0.95	0.28
Chromium	11	11	0.001	53	0.32	53	0.010	110	1.4	27	1.9
Cobalt	2.4	2.4	0.047	15	0.003	40	0.005	40	0.12	0.70	0.35
Copper	7.7	17	0.013	42	0.56	120	0.065	240	1.9	14	3.3
Dysprosium	1.2	1.5	--	4.2	--	8.4	--	4.2	0.035	<0.012	0.011
Erbium	0.16	0.16	--	1.1	--	1.0	--	0.48	0.012	<0.012	0.011
Europium	0.13	0.12	--	0.67	--	0.67	--	2.4	0.023	<0.012	0.011
Fluorine	66	130	0.50[3]	91	0.20[3]	91	0.031[3]	450	0.17	0.62	2.3
Gadolinium	0.14	0.27	--	0.69	--	1.6	--	1.0	0.046	<0.012	0.011
Gallium	0.86	0.86	0.003	13	0.008	27	0.006	47	1.6	3.1	0.45
Germanium	1.2	1.2	0.007	2.8	0.004	14	0.003	14	0.91	1.2	1.2
Gold	--	--	--	--	--	--	--	--	<0.012	<0.012	0.011

NOTES: [1] Concentration in ppm weight in solids and μg/ml in liquids. WEP analysis in 10^{-8} lb/scf (60°F, 29.92" Hg).

[2] Blind duplicate analysis.

[3] Possibly inaccurate due to loss from acidic solution.

[4] Approximate value only due to interference from preservative.

[5] Insufficient sample for determination.

--All elements not reported <0.1 ppm weight in solids or <0.001 μg/ml in liquids.

Maj. - Major component.

TABLE 4-4: STATION III, ANALYTICAL RESULTS BY SS-MS[1] (cont.)

Elements	Coal[2]		Inlet Ash Sluice Water	Bottom Ash	Bottom Ash Sluice Water	Economizer Ash	Economizer Ash Sluice Water	Cyclone Ash	South Duct WEP[2]		North Duct WEP
Hafnium	0.25	0.34	--	5.7	--	2.7	--	5.7	<0.012	<0.012	0.011
Holmium	0.04	0.08	--	0.31	--	0.31	--	0.31	<0.012	<0.012	0.011
Iodine	1.3	1.3	--	0.36	0.026	1.2	0.001	0.60	<0.012	<0.012	0.011
Iridium	--	--	--	--	--	--	--	--	<0.012	<0.012	0.011
Iron	>1%	>0.5%	0.55	>1%	3.3	>1%	2.6	>1%	~880	~700	200
Lanthanum	2.0	4.3	0.010	8.7	0.014	17	0.002	8.7	0.13	0.13	0.033
Lead	0.48	0.96	0.009	0.80	0.15	40	0.005	40	0.31	1.9	0.11
Lithium	7.3	13	0.012	71	0.016	400	0.022	860	0.13	0.24	0.022
Lutetium	0.05	0.05	--	0.44	--	0.29	--	0.15	<0.012	<0.012	0.011
Magnesium	>1%	>1%	24	>1%	25	>1%	24	>1%	310	300	190
Manganese	44	44	0.12	~2500	0.43	~3300	0.12	~1200	3.8	37	5.1
Mercury	--	--	[5]	--	[5]	--	[5]	--	[5]	[5]	[5]
Molybdenum	3.3	7.7	0.014	35	0.018	17	0.014	74	0.37	2.4	1.0
Neodymium	11	11	0.005	54	0.009	130	--	54	0.12	0.070	0.075
Nickel	14	2.8	0.18	28	0.046	28	0.036	49	1.0	56	1.3
Niobium	2.7	2.7	0.001	18	--	18	--	18	0.081	0.10	0.075
Osmium	--	--	--	--	--	--	--	--	<0.012	<0.012	0.011
Palladium	--	--	--	--	--	--	--	--	<0.012	<0.012	0.011
Phosphorus	70	70	0.086	960	0.64	960	0.14	960	6.0	Maj	28
Platinum	--	--	--	--	--	--	--	--	<0.012	<0.012	0.011
Potassium	~1200	560	18	~4800	18	~4800	18	~2400	200	190	180
Praseodymium	3.5	1.8	--	4.9	--	11	--	4.8	0.023	0.035	0.011
Rhenium	--	--	--	--	--	--	--	--	0.070	<0.012	0.011
Rhodium	--	--	--	--	--	--	--	--	<0.012	<0.012	0.011
Rubidium	0.98	3.5	0.019	4.0	0.052	23	0.041	23	2.9	1.7	3.9

NOTES:

[1] Concentration in ppm weight in solids and μg/ml in liquids. WEP analysis in 10^{-8} lb/scf (60°F, 29.92" Hg).
[2] Blind duplicate analysis.
[3] Possibly inaccurate due to loss from acidic solution.
[4] Approximate value only due to interference from preservative.
[5] Insufficient sample for determination.
--All elements not reported <0.1 ppm weight in solids or <0.001 μg/ml in liquids.
Maj. - Major component.

TABLE 4-4: STATION III, ANALYTICAL RESULTS BY SS-MS[1] (cont.)

Elements	Coal[2]		Inlet Ash Sluice Water	Bottom Ash	Bottom Ash Sluice Water	Economizer Ash	Economizer Ash Sluice Water	Cyclone Ash	South Duct WEP[2]		North Duct WEP
Ruthenium	--	--	--	--	--	--	--	--	<0.012	<0.012	0.011
Samarium	0.36	0.19	--	0.83	--	1.9	--	1.9	<0.012	<0.012	0.011
Scandium	5.3	2.9	--		--	16	--	34	<0.012	<0.012	0.011
Selenium	1.8	4.0	0.042	1.9	0.024	4.3	0.043	8.7	0.73	17	1.4
Silicon	>1%	>1%	3.3	>1%	20	>1%	4.2	>1%	Maj	Maj	Maj
Silver	0.26	0.13	0.002	1.4	0.024	0.28	0.002	0.28	0.023	1.3	0.011
Sodium	>1%	>1%	130	>1%	130	>1%	130	>1%	350	360	330
Strontium	310	620	1.4	~2800	3.1	~7800	3.8	~9700	39	28	0.52
Sulfur	>1%	>1%	Maj.	~1900	Maj.	>1%	Maj.	>1%	Maj	Maj	Maj
Tantalum	--	--	0.003	2.6	0.002	1.2	0.001	1.2	0.012	0.046	0.022
Tellurium	0.11	0.10	0.002	0.52	--	0.16	--	0.16	0.023	0.17	0.011
Terbium	0.10	0.09	--	0.53	--	0.53	--	0.80	<0.012	<0.012	0.011
Thallium	<0.12	<0.12	--	<0.10	0.003	<0.10	--	0.80	<0.012	0.34	0.011
Thorium	1.2	1.2	--	13	--	13	--	13	<0.012	<0.012	0.011
Thulium	0.07	0.07	--	0.26	--	0.26	--	0.12	<0.012	<0.012	0.011
Tin	1.8	0.80	0.003	2.0	0.050	2.0	--	4.6	0.45	15	3.0
Titanium	490	490	0.097	~2300	0.18	~1900	0.14	~4900	22	75	20
Tungsten	2.8	3.7	0.007	16	0.003	37	0.002	37	0.12	0.15	0.033
Uranium	1.2	0.54	--	11	0.002	11	--	11	0.035	0.058	0.032
Vanadium	10.2	19	0.008	85	0.010	85	0.031	180	1.3	45	3.1
Ytterbium	0.29	0.22	--	2.1	--	2.1	--	1.0	<0.012	<0.012	0.011
Yttrium	4.0	9.5	0.001	43	0.002	75	0.001	120	0.81	0.10	0.10
Zinc	0.38	0.95	0.079	2.0	1.0	4.3	0.080	55	2.0	28	5.9
Zirconium	9.5	14	0.003	62	0.004	62	0.001	110	1.5	0.20	0.21

NOTES:
[1] Concentration in ppm weight in solids and µg/ml in liquids. WEP analysis in 10^{-6} lb/scf (60°F, 29.92" Hg).
[2] Blind duplicate analysis.
[3] Possibly inaccurate due to loss from acidic solution.
[4] Approximate value only due to interference from preservative.
[5] Insufficient sample for determination.
--All elements not reported <0.1 ppm weight in solids or <0.001 µg/ml in liquids.
Maj. - Major component.

TABLE 4-5

TRACE ELEMENT FLOWS* AND MATERIAL BALANCE RESULTS AROUND STATION III (8/29/74)

Element	Coal	Ash Sluice Water	Σ In	Bottom Ash	Bottom Ash Sluice Water	Economizer Ash	Economizer Ash Sluice Water	Cyclone Ash	Flue Gas South Duct	Flue Gas North Duct	Σ Out	Σ Out/Σ In
Aluminum	1740	0.11	1740 ± 229	1480	.30	13.	.05	463	164	82	2200 ± 260	1.26
Antimony	.094	.0048	.10 ± .02	.013	.0061	.00008	.0018	.0049	.040	.025	.09 ± .01	.90
Arsenic	1.9	.0016	1.9 ± .3	.33	.0015	.019	.0001	1.2	.15	.25	1.9 ± .2	1.00
Barium	102	< .13	103 ± 23	96	< .089	1.3	< .044	48.	< 1.3	< 1.0	147 ± 26	1.43
Beryllium	.14	.0004	.14 ± .02	.089	.0003	.0014	.0003	.052	.006	.004	.15 ± .02	1.07
Boron	36	.07	36 ± 5	8.7	.045	.11	.21	10.	16.	6.4	42 ± 3	1.17
Cadmium	.046	.00007	.046 ± .007	.015	.0002	.0003	.0001	.018	.012	.011	.056 ± .005	1.22
Calcium	3220	9	3230 ± 330	2180	8.	18.	4.	816.	397.	204.	3630 ± 340	1.12
Chlorine	13	3.2	16 ± 2	1.5	2.8	.02	1.5	.84	6.4	8.0	21 ± 2	1.31
Chromium	3.1	<.014	3.1 ± .4	1.6	<.0094	.019	< .0046	.54	.78	.68	3.6 ± .4	1.16
Cobalt	.18	.00007	.18 ± .02	.17	.0007	.0018	.0003	.081	.062	.039	.35 ± .03	1.94
Copper	2.5	.002	2.5 ± .4	.84	.002	.014	.0007	.90	.42	.29	2.5 ± .2	1.00
Fluorine	13.	.05	13 ± 2	<.17	.044	.01	.02	4.2	6.4	6.1	17 ± 2	1.31
Iron	1770	.11	1770 ± 210	1100	.4	10	.12	358	2.08	103	1780 ± 180	1.01
Lead	.20	.0040	.21 ± .04	<.013	.0043	.0013	.0022	.051	.062	.062	.20 ± .02	.95
Magnesium	870	7	880 ± 90	623	4.6	5.8	2.1	226	100	49	1010 ± 100	1.15
Manganese	18	.022	18. ± 2	12	.0098	.14	.0084	4.7	1.6	.8	19 ± 2	1.06
Mercury	.017	<.0001	.017 ± .002	<.0002	<.00008	.00001	< .00004	.0011	.018	.016	.036 ± .004	2.12
Molybdenum	.46	.0087	.47 ± .08	.30	.0028	.0068	.0010	.38	.46	.70	1.9 ± .2	4.04
Nickel	1.3	.0016	1.3 ± .2	.39	.0002	.0055	.0006	.24	.52	.56	1.7 ± .2	1.31
Selenium	.31	.0003	.31 ± .03	.0042	.0002	.00002	.0001	.059	.070	.049	.18 ± .01	.58
Silver	.0079	<.00006	.008 ± .001	.0018	<.00004	.0004	<.00002	.0047	<.0007	<.0006	.0078 ± .0007	.98
Sulfur	3380	18	3400 ± 340	1.6	13.	.20	6.7	54.	1560	1390	3020 ± 300.	.89
Titanium	82.	<.027	82 ± 10	59	<.018	.59	<.0087	19.	3.4	3.3	85 ± 10	1.04
Uranium	.36	.0006	.36 ± .04	.054	.0006	.0017	.0004	.075	.034	.016	.18 ± .02	.50
Vanadium	3.5	<.0013	3.5 ± .5	2.4	<.0009	.017	<.0004	.54	.57	.41	3.9 ± .4	1.11
Zinc	1.8	.0034	1.8 ± .3	.30	.0023	.022	.0024	.75	.78	.41	2.3 ± .3	1.28

*All flow rates in lb/hr.

TABLE 4-6 - TRACE ELEMENT FLOWS* AND MATERIAL BALANCE RESULTS AROUND STATION III FROM SPARK SOURCE MASS SPECTROMETRY ANALYSES

ELEMENT	COAL	ASH SLUICE H_2O	Σ IN	BOTTOM ASH	BOTTOM ASH SLUICE H_2O	ECON ASH	ECON ASH SLUICE H_2O	CYCLONE ASH	FLUE GAS SOUTH DUCT	FLUE GAS NORTH DUCT	Σ OUT
ALUMINUM	410	0.32	410	>168	0.13	>1.5	0.10	>62	62	8	>300
ANTIMONY	0.095	<.0003	0.095	0.042	0.0005	0.0004	<0.00008	0.016	0.052	0.014	0.13
ARSENIC	1.8	0.0013	1.8	0.20	0.0021	0.0088	0.0017	0.75	0.42	0.11	1.5
BARIUM	88	0.082	88	12	0.071	~0.40	0.27	~11	1.0	0.43	~25
BERYLLIUM	0.61	<0.0003	0.61	0.94	<0.0002	0.0017	<0.00006	0.069	0.0026	0.0021	1.0
BISMUTH	<0.19	<0.0003	<0.19	<0.0029	<0.0002	0.0005	<0.00008	0.0093	0.010	0.0021	0.025
BORON	59	<0.027	59	~17	<0.018	~0.34	<0.0087	~16	--	4.1	~37
BROMINE	0.72	0.0066	0.72	0.052	0.012	0.0035	0.0010	0.034	0.023	0.0041	0.13
CADMIUM	0.56	0.0077	0.57	0.022	0.066	0.0004	0.0025	0.0081	1.3	0.19	1.6
CALCIUM	>2560	8.7	>2570	>168	7.3	>1.5	4.1	>62	234	140	>620
CERIUM	3.1	0.0013	3.1	0.67	0.0004	0.011	0.00008	0.44	0.055	0.035	1.2
CESIUM	0.059	0.0003	0.059	0.0072	0.0011	0.0002	0.00008	0.027	0.029	0.064	0.13
CHLORINE	26	0.05	26	0.44	0.36	0.014	0.032	0.32	0.15	0.052	1.4
CHROMIUM	2.6	0.0003	2.6	0.89	0.057	0.0082	0.0009	0.69	3.1	0.35	5.1
COBALT	0.56	0.012	0.58	0.25	0.0005	0.0062	0.0004	0.25	0.091	0.066	0.67
COPPER	3.1	0.0034	3.1	0.71	0.10	0.018	0.0057	1.5	1.8	0.62	4.7
DYSPROSIUM	0.33	<0.0003	0.33	0.071	<0.0002	0.0013	<0.00008	0.026	0.0078	<0.0021	0.11
ERBIUM	0.038	<0.0003	0.039	0.018	<0.0002	0.0002	<0.00008	0.0030	0.0026	<0.0021	0.027
EUROPIUM	0.031	<0.0003	0.031	0.011	<0.0002	0.0001	<0.00008	0.015	0.0052	<0.0021	0.034
FLUORINE	23	0.13	23	1.5	0.036	0.014	0.0027	2.8	0.088	0.43	4.9
GADOLINIUM	0.049	<0.0003	0.049	0.012	<0.0002	0.0002	<0.00008	0.0062	0.010	<0.0021	0.031
GALLIUM	0.20	0.0008	0.20	0.22	0.0014	0.0042	0.0005	0.29	0.55	0.84	1.1
GERMANIUM	0.28	0.0019	0.28	0.047	0.0007	0.0022	0.0003	0.087	0.23	0.23	0.60
GOLD	<0.026	<0.0003	<0.026	<0.0017	<0.0002	<0.00001	<0.00008	<0.0006	<0.0026	<0.0021	<0.0072
HAFNIUM	0.069	<0.0003	0.069	0.096	<0.0002	0.0004	<0.00008	0.036	<0.0026	<0.0021	0.14
HOLMIUM	0.015	<0.0003	0.016	0.0052	<0.0002	0.00004	<0.00008	0.0019	<0.0026	<0.0021	0.012
IODINE	0.31	<0.0003	0.31	0.0060	0.0046	0.0002	0.00008	0.0037	<0.0026	<0.0021	0.019
IRIDIUM	<0.026	<0.0003	<0.026	<0.0017	<0.0002	<0.00001	<0.00008	<0.0006	<0.0026	<0.0021	<0.0072
IRON	>1792	0.15	>1790	>168	0.59	>1.5	0.23	>62	179	37	>450
LANTHANUM	0.74	0.0027	0.74	0.15	0.0025	0.0026	0.0002	0.054	0.029	0.0062	0.24
LEAD	0.17	0.0024	0.17	0.013	0.027	0.0062	0.0004	0.25	0.24	0.021	0.56
LITHIUM	2.4	0.0032	2.4	1.2	0.0028	0.062	0.0019	5.4	0.042	0.0041	6.7
LUTETIUM	0.013	<0.0003	0.013	0.0074	<0.0002	0.00004	<0.00008	0.0009	<0.0026	<0.0021	0.013
MAGNESIUM	>2560	6	>2570	>168	4.5	>1.5	2.1	>62	70	35	>340
MANGANESE	10	0.032	10	~42	0.077	~0.51	0.010	~7.5	4.7	0.95	~56

* All flows in lb/hr.

TABLE 4-6 - TRACE ELEMENT FLOWS* AND MATERIAL BALANCE RESULTS AROUND STATION III FROM SPARK SOURCE MASS SPECTROMETRY ANALYSES (Cont.)

ELEMENT	COAL	ASH SLUICE H_2O	Σ IN	BOTTOM ASH	BOTTOM ASH SLUICE H_2O	ECON ASH	ECON ASH SLUICE H_2O	CYCLONE ASH	FLUE GAS SOUTH DUCT	FLUE GAS NORTH DUCT	Σ OUT
MERCURY	<0.026	--	<0.026	<0.0017	--	<0.00001	--	<0.0006	--	--	<0.0023
MOLYBDENUM	1.3	0.0037	1.3	0.59	0.0032	0.0026	0.0012	0.46	0.70	0.19	2.0
NEODYMIUM	2.6	0.0013	2.6	0.91	0.0016	0.020	<0.00008	0.34	0.021	0.014	1.3
NICKEL	2.9	0.068	2.9	0.47	0.0082	0.0043	0.0031	0.31	6.2	0.25	7.3
NIOBIUM	0.64	0.0003	0.64	0.30	<0.0002	0.0028	<0.00008	0.11	0.021	0.014	0.45
OSMIUM	<0.026	<0.0003	<0.026	<0.0017	<0.0002	<0.00001	<0.00008	<0.0006	<0.0026	<0.0021	<0.0072
PALLADIUM	<0.026	<0.0003	<0.026	<0.0017	<0.0002	<0.00001	<0.00008	<0.0006	<0.0026	<0.0021	<0.0072
PLATINUM	<0.026	<0.0003	<0.026	<0.0017	<0.0002	<0.00001	<0.00008	<0.0006	<0.0026	<0.0021	<0.0072
POTASSIUM	205	4.8	210	~81	3.2	~7.4	1.6	~15	42	33	~180
PRASEODYMIUM	0.61	<0.0003	0.61	0.082	<0.0002	0.0017	<0.00008	0.030	0.0078	0.0021	0.12
RHENIUM	<0.026	<0.0003	<0.026	<0.0017	<0.0002	<0.00001	<0.00008	<0.0006	<0.0026	<0.0021	<0.0072
RHODIUM	<0.026	<0.0003	<0.026	<0.0017	<0.0002	<0.00001	<0.00008	<0.0006	<0.0026	<0.0021	<0.0072
RUBIDIUM	0.54	0.0050	0.54	0.067	0.0093	0.0035	0.0036	0.14	0.52	0.72	1.5
RUTHENIUM	<0.026	<0.0003	<0.026	<0.0017	<0.0002	<0.00001	<0.00008	<0.0006	<0.0026	<0.0021	<0.0072
SAMARIUM	0.064	<0.0003	0.064	0.014	<0.0002	0.0003	<0.00008	0.012	<0.0026	<0.0021	0.031
SCANDIUM	0.97	<0.0003	0.97	1.3	<0.0002	0.0025	<0.00008	0.21	<0.0026	<0.0021	1.6
SELENIUM	0.69	0.011	0.70	0.032	0.0043	0.0007	0.0037	0.054	2.0	0.27	2.4
SILVER	0.046	0.0005	0.047	0.024	0.0043	0.00004	0.0002	0.0017	0.16	<0.0021	0.19
SODIUM	>2560	34	>2590	>168	23	>1.5	11	>62	78	62	>410
STRONTIUM	110	0.37	110	~47	0.55	~1.2	0.33	~60	7.5	9.7	~130
TANTALUM	<0.026	0.0008	<0.026	0.044	0.0004	0.0002	0.00008	0.0075	0.0078	0.0041	0.064
TELLURIUM	0.026	0.0005	0.026	0.0087	<0.0002	0.00002	<0.00008	0.0010	0.023	0.0021	0.035
TERBIUM	0.023	<0.0003	0.023	0.0089	<0.0002	0.00008	<0.00008	0.0050	<0.0026	<0.0021	0.019
THALLIUM	<0.028	<0.0003	<0.028	<0.0017	0.0005	<0.00001	<0.00008	0.0050	0.075	<0.0021	0.085
THORIUM	0.28	<0.0003	0.28	0.22	<0.0002	0.0020	<0.00008	0.081	<0.0026	0.0021	0.31
THULIUM	0.015	<0.0003	0.016	0.0044	<0.0002	0.00004	<0.00008	0.0007	<0.0026	<0.0021	0.010
TIN	0.31	0.0008	0.31	0.034	0.0089	0.0003	<0.00008	0.029	1.7	0.56	2.4
TITANIUM	115	0.026	115	~39	0.032	~0.29	0.012	~31	11	3.7	~84
TUNGSTEN	0.77	0.0019	0.77	0.27	0.0005	0.0057	0.0002	0.23	0.031	0.0062	0.54
URANIUM	0.20	<0.0003	0.21	0.18	0.0004	0.0017	<0.00008	0.069	0.010	0.006	0.27
VANADIUM	3.3	0.0021	3.3	1.4	0.0018	0.013	0.0027	1.1	5.2	0.56	8.3
YTTERBIUM	0.059	<0.0003	0.059	0.035	<0.0002	0.0003	<0.00008	0.0062	<0.0026	<0.0021	0.047
YTTRIUM	1.6	0.0003	1.6	0.72	0.0004	0.012	0.00008	0.75	0.10	0.019	1.6
ZINC	0.16	0.021	0.18	0.034	0.18	0.0007	0.0070	0.34	3.4	1.1	5.1
ZIRCONIUM	4.4	0.0008	4.4	1.0	0.0007	0.0095	0.00008	0.69	0.21	0.039	2.0

* All flows in lb/hr.

of all incoming streams, coal and ash sluice water, are given as Σ In. The flow rates of the outgoing streams, bottom ash, bottom ash sluice water, cyclone ash, flue gas south duct and flue gas north duct, also were added and are listed as Σ Out. The error limits given were calculated from the estimated errors in the analyses and the estimated errors in the flows according to the procedures described in Section 3.0.

The emission results for sulfur and particulates are summarized in Table 4-7 since these are the two emission parameters of greatest immediate importance. The results are provided on a lb/BTU basis to facilitate comparison to other stations.

TABLE 4-7

EMISSION RESULTS FOR PARTICULATES AND SULFUR DIOXIDE AT STATION III

	Particulates (Ash)	Sulfur Dioxide
Concentration in flue gas		
North Duct	0.50 gr/scf	880 ppm (v/v)
South Duct	0.65 gr/scf	830 ppm (v/v)
Quantity in coal per unit heat value	12.6 lb/10^6 BTU	2.93 lb/10^6 BTU
Emissions in flue gas per unit heat value of coal burned	1.5 lb/10^6 BTU	2.56 lb/10^6 BTU

5.0 DISCUSSION OF RESULTS

Two areas are of primary interest regarding the results presented in Section 4.0. The first is the trace element levels and their distribution among the exit streams; the second is the level of confidence of the data as indicated by material balance closure.

5.1 Material Balance Closure

The criteria used for judging overall reliability of the data are the degree of closure of the material balances. Closure within error limits, indicated by an overlap of the error bands for Σ In and Σ Out presented in Table 4-5, lends support to the reliability of the individual element flows. The balances close within error limits for the following 21 elements.

Aluminum
Antimony
Arsenic
Barium
Beryllium
Boron
Cadmium
Calcium
Chromium
Copper
Fluorine
Iron
Lead
Magnesium
Manganese
Nickel
Silver
Sulfur
Titanium
Vanadium
Zinc

The balance for chlorine is slightly out of the limits (16 ± 2 lbs/hr in versus 21 ± 2 lbs/hr out). Larger variations are found for:

Cobalt	.18 ± .02 lbs/hr in	.35 ± .03 lbs/hr out
Mercury	.017 ±.002 lbs/hr in	.036 ±.004 lbs/hr out
Molybdenum	.47 ± .08 lbs/hr in	1.9 ± .2 lbs/hr out
Selenium	.31 ± .03 lbs/hr in	.18 ± .01 lbs/hr out
Uranium	.36 ± .04 lbs/hr in	.18 ± .02 lbs/hr out

The nonclosure of these balances may be attributed to errors in sampling, sample handling or sample analysis. Selenium, mercury and chlorine present special sampling difficulties since they may be present in the gaseous phase. The degree of closure of the balances obtained by the quantitative analytical techniques and by spark source mass spectrometry are compared in Table 5-1. For each element a normalized deviation was calculated according to:

$$ND(j) = \frac{\Sigma in(j) - \Sigma out(j)}{(\Sigma in(j) + \Sigma out(j))/2} \qquad (5\text{-}1)$$

The average of the normalized deviations was -0.14 for the quantitative methods and -0.29 for the SSMS results, indicating that the exit flows of the trace constituents were measured on the average higher than the incoming flows. The root mean square of the normalized deviations according to

$$RMS_{ND} = \left[\frac{1}{n} \sum_{j} \left(\frac{\Sigma in(j) - \Sigma out(j)}{\frac{\Sigma in(j) + \Sigma out(j)}{2}} \right)^{2} \right]^{\frac{1}{2}} \qquad (5\text{-}2)$$

are 0.37 for the quantitative methods and 1.1 for the SSMS results. The RMS over 53 elements for SSMS was 0.87. Results less than or greater than a certain value were not included in the latter calculations. These deviation calculations provide some measure of the overall material balance closure for each of the two analytical approaches.

5.2 Distribution of Elements in the Exit Streams

The incoming ash is distributed among the exit ashes as follows:

TABLE 5-1

DEVIATIONS FROM MATERIAL BALANCE CLOSURE FOR QUANTITATIVE ANALYSES AND SPARK SOURCE MASS SPECTROMETRIC ANALYSES

Elements	Quantitative Normalized[1] Deviation	SSMS Normalized[1] Deviation
Aluminum	-0.23	--
Antimony	0.11	-0.31
Arsenic	0	0.18
Barium	-0.35	1.12
Beryllium	-0.069	-0.48
Boron	-0.15	0.46
Cadmium	-0.20	-0.95
Calcium	-0.12	--
Chlorine	-0.27	1.80
Chromium	-0.15	-0.65
Cobalt	-0.64	-0.14
Copper	0	-0.41
Fluorine	-0.27	1.30
Iron	-0.0056	--
Lead	0.049	-1.07
Manganese	-0.054	-1.39
Magnesium	-0.14	--
Mercury	-0.72	--
Molybdenum	-1.21	-0.42
Nickel	-0.27	-1.14
Selenium	0.53	-1.10
Silver	0.025	-1.21
Sulfur	0.12	--
Titanium	-0.036	0.31
Uranium	0.67	-0.25
Vanadium	-0.11	-0.86
Zinc	-0.24	-0.93
Average of Normalized Deviations	-0.14	-0.29
RMS of Deviations[2]	0.37	1.1

NOTES:

1. Normalized Deviation = $\dfrac{\Sigma_{in}(j) - \Sigma_{out}(j)}{\left(\dfrac{\Sigma_{in}(j) + \Sigma_{out}(j)}{2}\right)}$

2. Root Mean Square of Normalized Deviations = $\sqrt{\dfrac{\sum_j \left[\dfrac{\Sigma_{in}(j) - \Sigma_{out}(j)}{\left(\dfrac{\Sigma_{in}(j) + \Sigma_{out}(j)}{2}\right)}\right]^2}{n}}$

Bottom Ash	63.1%
Economizer Ash	0.6%
Cyclone Ash	23.4%
Fly Ash	12.9%

The trace constituents entering the plant with the coal would, in the simplest case, leave the plant in the same ratios as the ashes. This will be the case, however, only if no mechanism in the boiler leads to a preferential concentration in one of the exit streams. Potential enrichment mechanisms are

1) volatilization of an element or compound and

2) chemical changes with formation of a volatile element or compound.

The elements or compounds which vaporize can subsequently

1) leave the plant without recondensation,
2) recondense partially, or
3) recondense completely.

Those elements that are vaporized in the boiler are subsequently enriched in the economizer ash, cyclone ash or flue gas. The relative distribution in these streams is a function of the degree of recondensation that occurs. The volatile components that do not recondense are discharged primarily with the flue gas. Condensation on the surface of available particulate matter will result in a particular relative abundance of a given element in the various ash streams dependent on the particulate size distribution in each stream and the degree of recondensation.

The element distribution in the bottom ash, in the combined economizer and cyclone ash and in the flue gas for the 27 constituents quantitatively analyzed is shown on a percent basis in Table 5-2. The values for bottom ash and economizer ash were corrected for losses by leaching during the sluicing operation. This correction was made by assuming that any increase in concentration of a trace element in the liquid portion of the bottom ash or economizer ash sluice stream was due to leaching of that element from the respective ash. The concentration difference (increase) between the inlet and outlet water streams was converted to elemental mass flow using the outlet bottom ash and economizer ash sluice water flows and added to the mass flow in the ash solids. This total elemental mass flow in the ashes was then used to calculate the distribution shown in Table 5-2. The corrections were in most cases insignificant.

The second column of Table 5-2 gives the total flow in the coal of an incoming trace element in lbs/hr. The third column is the portion in percent of the total outgoing flow of an element found in the bottom ash. Values higher than 63.1% indicate an enrichment of an element in the bottom ash; values lower than 63.1%, a depletion. The remaining columns present the fractions in the other ash streams and the same reasoning holds true for the economizer ash (gross average 0.6%), the cyclone ash (gross average 23.4%), and the flue gas (gross average 12.9%). Values for an element higher than these averages again indicate an enrichment; values lower than these values, a depletion.

The results shown in Table 5-2 are graphically displayed in Figure 5-1. The elements are approximately ordered according to descending enrichment in the flue gas. The gross average values for total fly ash (12.9%), cyclone plus economizer

TABLE 5-2

DISTRIBUTION OF ELEMENTS AMONG BOTTOM ASH, ECONOMIZER ASH CYCLONE ASH AND FLUE GAS AT STATION III

ELEMENT	lb/hr in coal	BOTTOM ASH % (AVERAGE 63.1)	ECONOMIZER ASH % (AVERAGE 0.6%)	CYCLONE ASH % (AVERAGE 23.4%)	FLUE GAS % (AVERAGE 12.9%)
ALUMINUM	1740	67.2	0.6	21.0	11.2
ANTIMONY	0.094	15.9	0.3	5.9	77.9
ARSENIC	1.9	16.9	1.0	61.6	20.5
BARIUM	102	64.9	0.9	32.4	< 1.6
BERYLLIUM	0.14	58.2	1.0	34.0	6.5
BORON	36	21.0	0.7	24.1	54.1
CADMIUM	0.046	26.8	0.4	32.1	41.1
CALCIUM	3220	60.3	0.5	22.6	16.6
CHLORINE	13	12.2	2.9	4.7	80.0
CHROMIUM	3.1	44.2	0.5	14.9	40.3
COBALT	0.18	48.0	0.5	22.9	28.5
COPPER	2.5	34.1	0.6	36.6	28.9
FLUORINE	13	< 1.1	0.06	24.9	74.0
IRON	1770	61.8	0.6	20.1	17.5
LEAD	0.20	< 7.8	1.1	26.6	64.6
MANGANESE	13	62.5	0.7	24.5	12.5
MAGNESIUM	870	62.1	0.6	22.5	14.8
MERCURY	0.017	< 0.8	0.03	3.1	96.1
MOLYBDENUM	0.46	16.3	0.3	20.6	63.0
NICKEL	1.3	22.7	0.3	14.0	62.8
SELENIUM	0.31	2.3	0.01	32.4	65.4
SILVER	0.0079	22.0	4.9	57.3	<15.9
SULFUR	3380	0.09	0.03	1.8	98.1
TITANIUM	82	69.2	0.7	22.3	7.9
URANIUM	0.36	29.8	1.0	41.4	27.6
VANADIUM	3.5	60.9	0.4	13.7	24.9
ZINC	1.8	13.3	1.0	33.2	52.7

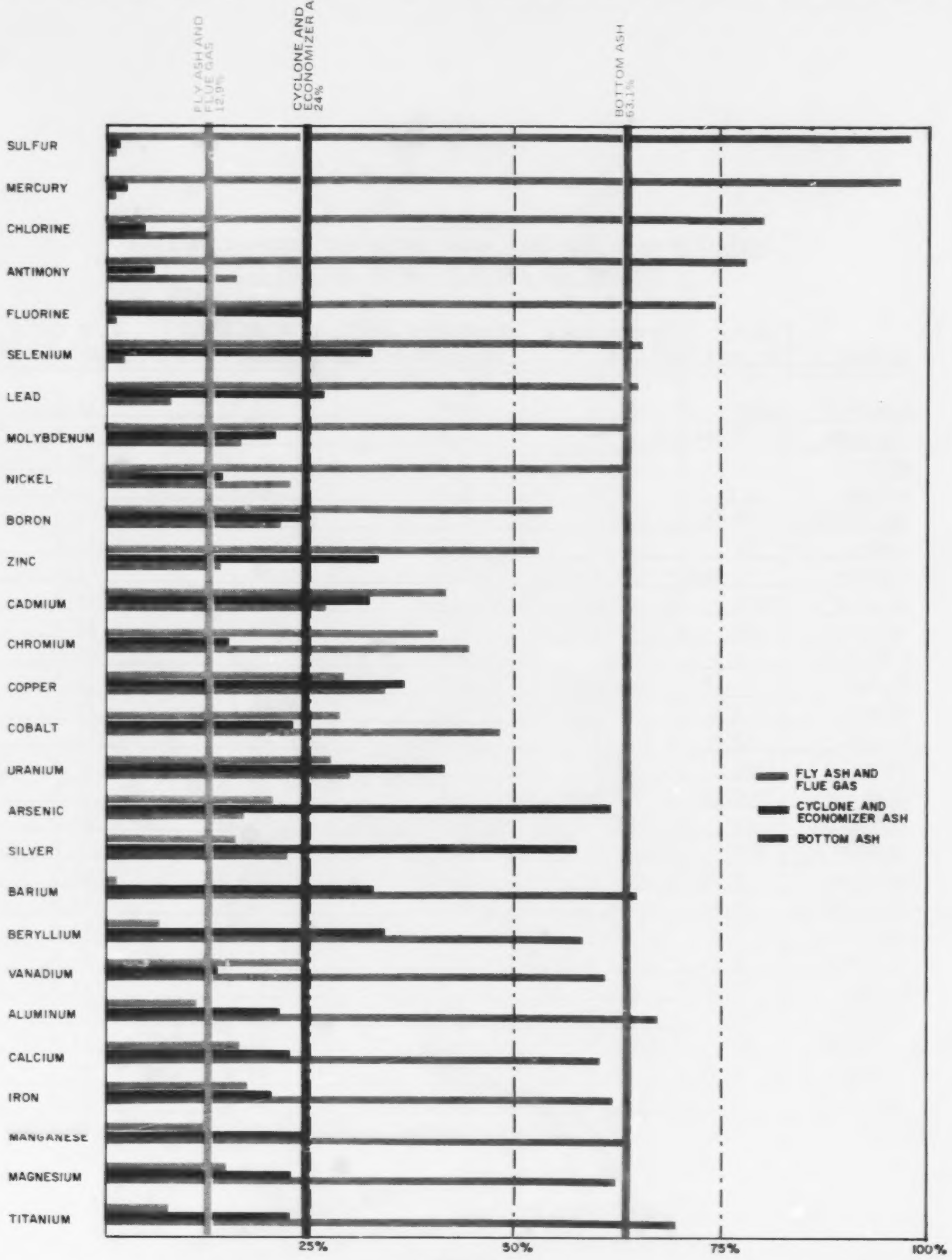

FIGURE 5.1
DISTRIBUTION OF THE TRACE ELEMENT
AMONG STATION III PLANT EXIT ASHES

[redacted] 252

ash (24%), and bottom ash (63.1%) are indicated as red, blue, and green vertical lines respectively. The concentration of each trace constituent in these three streams are given for each element as horizontal bars. The concentration in the fly ash plus flue gas on a percent basis is shown in red, the concentration of cyclone and economizer ash in blue, and the concentration in the bottom ash in green. The crossing of two lines of the same color indicates enrichment.

The elements can, according to Table 5-2 and Figure 5-2, roughly be divided into three broad classes. Class one contains the elements significantly enriched in the flue gas. They are, in descending order of enrichment:

1) Sulfur
2) Mercury
3) Chlorine
4) Antimony
5) Fluorine
6) Selenium
7) Lead
8) Molybdenum
9) Nickel
10) Boron
11) Zinc
12) Cadmium
13) Chromium
14) Copper
15) Cobalt

Material balances for four of the above elements, mercury, selenium, molybdenum, and cobalt, exceeded the error limits. The exact position of these elements in the above list may slightly vary. However, the general trend should hold even for these elements.

Class two elements seem to be enriched in the cyclone plus economizer ash. This class includes:

1) Uranium
2) Arsenic
3) Silver

The uranium material balance did not close within the stated limits. Chemical compound identification and determination of enrichment as a function of particle size would aid in clarifying the enrichment mechanisms exhibited by this class.

Class three includes the elements which are more of less evenly distributed among the ashes. These elements are:

1) Barium
2) Beryllium
3) Vanadium
4) Aluminum
5) Calcium
6) Iron
7) Manganese
8) Magnesium
9) Titanium

APPENDIX A
SAMPLING AT STATION III

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1.0 INTRODUCTION

Sampling at Station III was performed by Radian personnel during the period 26-30 August 1974. The station was selected as part of the Northern Great Plains Resources Program trace elements study to be representative of a plant with cyclone dust collectors for fly ash control and a lignite-fired boiler with cyclone burners.

Representative samples of all inlet and outlet streams around the power plant were collected with the objective of quantifying the trace element emissions from the plant. Analyses of the samples for the trace elements of interest in combination with flow rate data for each stream during the sample period allows a material balance to be performed for each element. These material balances serve two main functions: (1) closure of the material balance lends credibility to the sampling and analytical techniques and, therefore, to the emission data produced, and (2) data is generated which allows the ultimate fate of individual trace elements to be determined and their flow through the plant system to be traced.

The following sections provide descriptions of the station, the sampling techniques utilized and flow rate measurements performed.

2.0 PLANT DESCRIPTION

Station III consists of one 250 MW boiler which fires a medium sulfur lignite coal mined in an area immediately west of the plant site and trucked to the plant. Following crushing, the coal is conveyed to seven storage silos. The coal is reduced to a maximum size of one-fourth inch by mills prior to being fed to the cyclone burners in the furnace.

The bottom ash removal system consists of quench tanks where the melted ash is quenched in pond water and a sluice system to pump the bottom ash sluice to a storage basin. The economizer ash is also handled by the same sluice system and is pumped to the basin alternatively with the bottom ash.

The dust control system consists of six cyclone dust collectors where a portion of the ash in the flue gas is collected, stored in pressurized hoppers, and transferred pneumatically to a storage silo. The ash is periodically trucked away from the storage silo after wetting to prevent dusting.

A schematic of the Station III is shown in Figure 2-1.

2.1 Plant Operation During Sampling

The plant was run at a constant load of 245-250 MW during the entire sampling period. This consistency of operation allowed the collection of samples which were representative of the entire period and the averaging of flow rates for all streams over the sampling period.

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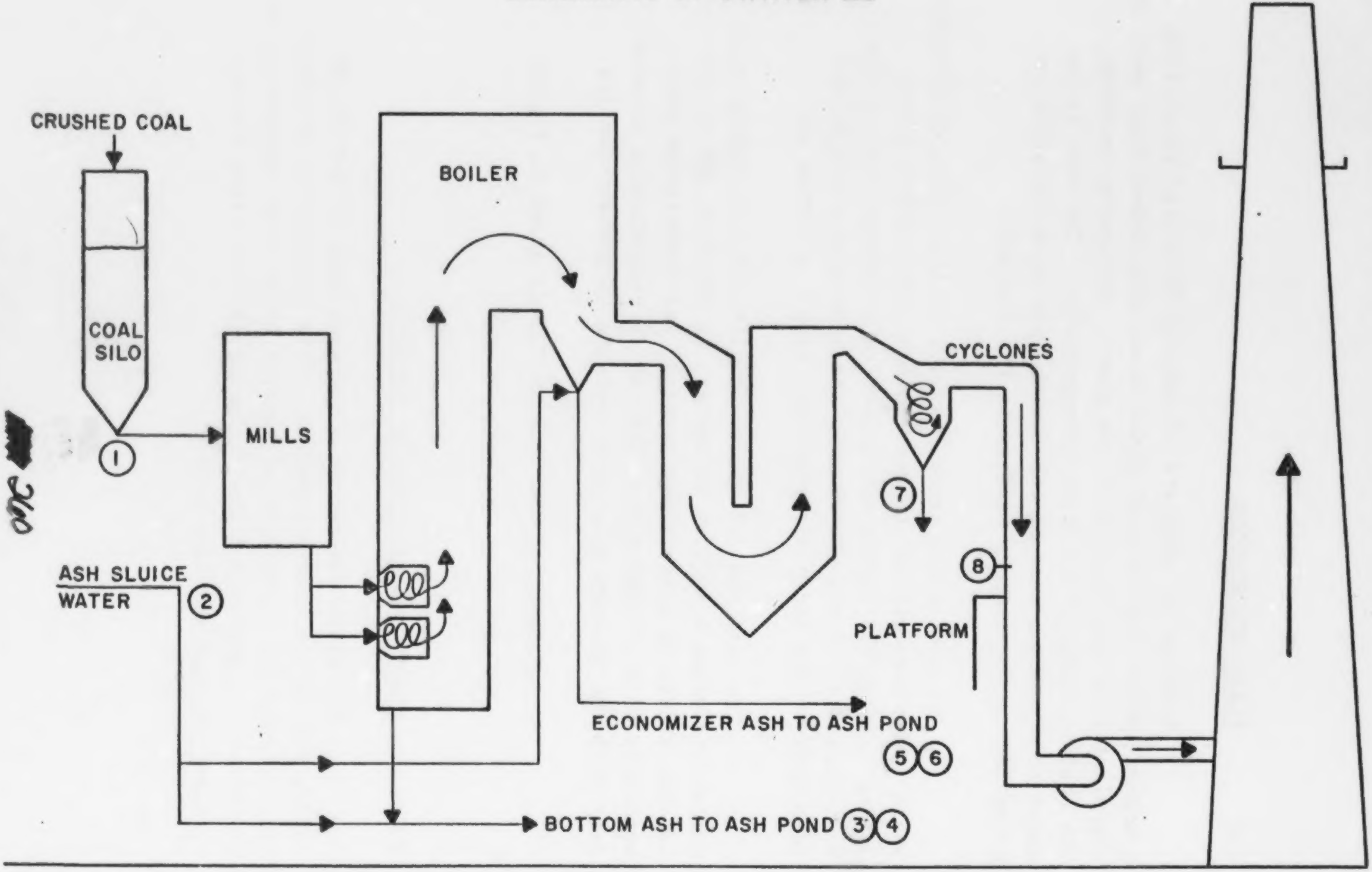
FIGURE 2-1
SCHEMATIC OF STATION III


CRUSHED COAL
COAL SILO
①
MILLS
ASH SLUICE WATER
②
BOILER
CYCLONES
⑦
⑧
PLATFORM
ECONOMIZER ASH TO ASH POND
⑤⑥
BOTTOM ASH TO ASH POND
③④

[redacted] 260

2.2 Time Phasing During Sampling

All of the streams flowed continuously with short residence times within the system with three exceptions. Bottom ash accumulated in a storage tank and was sluiced to the storage basin every four hours requiring 30 minutes to empty the tank. Economizer ash was allowed to accumulate in the economizer ash hopper for four hours after which the accumulation was sluiced to the storage basin over a period of 30 minutes. The only time phasing required for these two streams was to sample during the time when the ash which had accumulated during the sampling period was sluiced.

Cyclone ash was stored in a silo to await trucking. However, since the cyclone ash samples were taken from the cyclone ash hoppers at the base of each cyclone where the residence time was short, time phasing was unnecessary. Since the plant load was constant, the accumulation of cyclone ash in the storage silo could be averaged over a 48 hour period to give a reliable rate of cyclone ash production.

3.0 DESCRIPTION OF SAMPLING POINTS

The sample point locations are indicated in Figure 2-1 and the inlet and outlet streams in Figure 3-1. The following sections provide detailed descriptions of the sample points and the techniques employed to obtain samples representative of the sampling period.

3.1 Coal

Coal samples were taken from 2" diameter sampling ports in the transfer line between storage silos 2, 4, and 6 and the corresponding mills. The ports were closed with caps between samples and when uncapped coal flowed freely into a polyethylene collection bucket unless the port became obstructed by a large piece of coal. The first portion of this flow was discarded to insure a fresh sample each time and approximately two pounds retained. A coal sample was taken every 20 minutes from 9:00 AM to 5:00 PM, August 29, 1974, such that each port was sampled once every hour. The samples were combined in a large polyethylene container. This composite sample was quartered until two 1-liter polyethylene bottles of coal remained for analysis.

3.2 Bottom Ash and Economizer Ash Sluice Water Inlet

Plant service water from the plant lake is used to sluice bottom ash from the quench tanks and economizer ash from the economizer hopper. The service water is taken directly from the lake about 10 feet from shore and 100 feet from the inlet pump. A two liter sample was taken in a polyethylene container

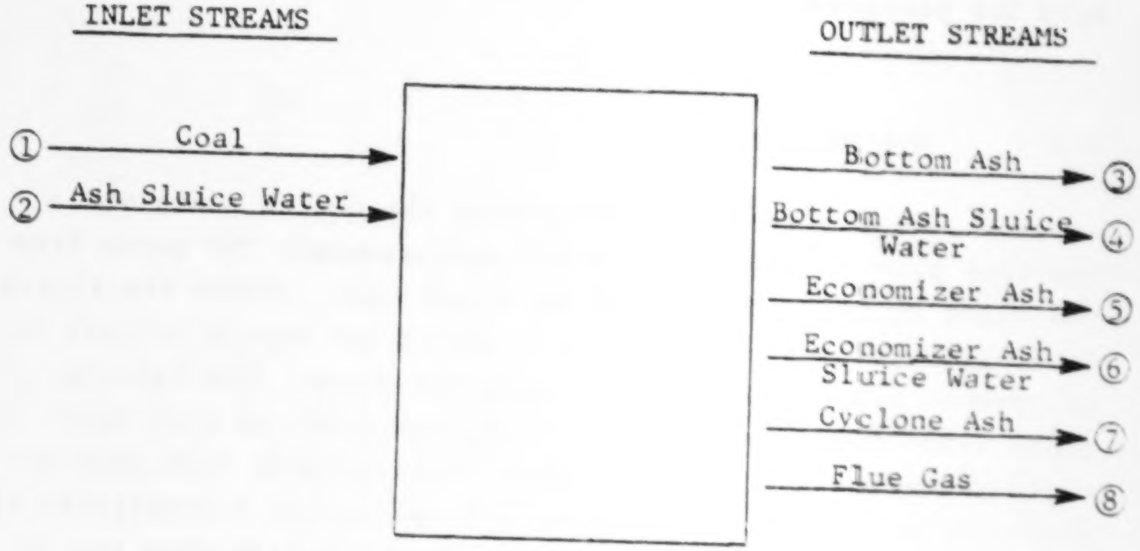

INLET STREAMS
OUTLET STREAMS
① Coal
② Ash Sluice Water
Bottom Ash ③
Bottom Ash Sluice Water ④
Economizer Ash ⑤
Economizer Ash Sluice Water ⑥
Cyclone Ash ⑦
Flue Gas ⑧

FIGURE 3-1

INLET AND OUTLET STREAMS
AT STATION III

at 4:00 PM on August 29th at the inlet and acidified with nitric acid for preservation.

3.3 Bottom Ash

Bottom ash was sluiced from the quench tanks via a ten inch pipe to a disposal basin approximately 300 yards from the plant at the upper end of the plant lake. There the sluice water flows into the lake and the bottom ash solids collect to be trucked away. Bottom ash sluice was pumped from holding tanks every four hours (10:30, 2:30, and 6:30) on a 24 hour basis until the holding tanks were emptied which took approximately 30 minutes. Representative sampling was accomplished by passing a hose sampling device through the stream from top to bottom and bottom to top every 2.5 minutes during the pumping time. This was necessary because the bottom ash solids were stratified in the effluent stream by settling dependent on particle size and density. The hose was inserted into a five gallon polyethylene container for the collection of the sample. Approximately five gallons of the solid-liquid sluice stream were collected during a pumping period. The solid-liquid mixture was filtered in the laboratory and the entire solid portion of the sample was retained.

3.4 Bottom Ash Sluice Water Outlet

The bottom ash sluice water outlet was collected with the bottom ash as described in Section 3.3. Two liters of the filtrate was acidified for preservation and retained in polyethylene bottles for analysis.

3.5 Economizer Ash

The economizer ash from the economizer ash hopper was sluiced with plant service water through the same system as the bottom ash. Sluicing took place every four hours (10:00, 2:00, and 6:00) on a 24 hour basis for approximately 30 minutes. Collection and handling of the samples was the same as that followed for the bottom ash. After filtration, the solids were retained for analysis.

3.6 Economizer Ash Sluice Water Outlet

The economizer ash sluice water outlet was collected with the economizer ash described in Section 3.5. Two liters of the filtrate were acidified for preservation and retained in polyethylene bottles for analysis.

3.7 Cyclone Ash

Ash from the cyclone dust collectors was collected from hoppers 1, 3, and 5 every hour from 10:00 AM to 5:00 PM on August 29, 1974. Since the hoppers were pressurized, the pneumatic ash transport system to the storage silo was shut down for five to ten minutes every hour for sample collection. Samples were obtained by removal of five inch glass observation windows in the hoppers and one to two liters of ash removed with a small scoop. The individual samples were combined in a large polyethylene container and riffled to yield two, one liter integral samples, one for analysis and one for reserve.

3.8 Flue Gas

Particulate matter in the exiting flue gas was sampled from two 12 ft. by 16 ft. ducts between the cyclone dust collectors and the induced draft fans. At this point there are four 4-inch diameter sampling ports in each duct to provide access to the flue gas stream. The flue gas was at a temperature of 375-380°F, static pressure of -17.5 in. H_2O, and 12.5% moisture during the sampling period.

For sampling purposes each duct was divided into 16 sections of equal areas as shown in Figure 3-2. The center point of each section was the actual sampling point and assumed to be representative of the section.

Velocity traverses of the two ducts were made on August 27th and in conjunction with the grain loading determinations on August 28th and 29th as per EPA Method 2. Figure 3-2 presents the average velocity at each sample point over the three-day period. The average velocity in the north duct was found to be 55 fps and in the south duct 67 fps. The velocity traverses determined the total gas flow in the duct and the conditions necessary for isokinetic sampling.

Particulate loading determinations were made with Gelman filter devices on August 27, 28, and 29th. The majority of the determinations were made on the 27th and 28th and those made on the 29th were to detect any significant deviations from the previous two days. Figure 3.3 presents the grain loading data taken. It should be noted that in many cases there are great differences between adjoining sections in both ducts and some sections have two grain load concentrations shown. This is due to the random blowing of soot from the boiler during the

NORTH DUCT

68	58	54	72	4
55	50	52	63	3
59	47	54	65	2
54	37	42	59	1
D	C	B	A	

SOUTH DUCT

77	66	66	77	4
77	67	62	78	3
66	63	62	79	2
60	54	56	63	1
D	C	B	A	

FIGURE 3-2

Velocity Profile (fps) at
Station III

NORTH DUCT

0.27	0.27	0.35	0.94	4
0.48	0.34	0.42	0.42	3
0.35	0.49	0.88 0.41	0.40	2
0.88	1.01 0.35	0.48	0.80	1
D	C	B	A	

SOUTH DUCT

0.60	0.35	0.93	0.54	4
0.81 0.45	0.43	0.38	0.32	3
0.53	1.15 0.36	0.41	0.51	2
0.61	0.57	1.00 0.52	1.55	1
D	C	B	A	

FIGURE 3-3

Grain Loading Profile (grains per scf)
Station III

sampling period. The lower concentrations (< 0.61 grains per scf) were apparently taken during periods when soot blowing was not taking place and the higher concentrations (> 0.80 grains per scf) were apparently taken during periods when soot blowing was taking place. The random nature of the soot blowing makes an exact analysis of the data difficult; however, the period of grain loading sampling on August 27th was of sufficient length for such random fluctuations to be taken into account if we take a time average of the grain loading data in each duct to calculate an average grain loading over the entire sampling period. This time averaging yields average particulate loads of 0.50 grains per scf for the north duct and 0.65 grains per scf for the south duct. During particulate loading determinations, the moisture content of the flue gas was measured by condensation in an efficient copper tubing condenser maintained in an ice bath.

Samples of the particulate matter in the flue gas stream for analysis were taken at Point C-2 in each duct on August 29th during the period when the other plant streams were sampled. The wet electrostatic precipitator (WEP) sampling system used for sample collection is shown schematically in Figure 3-4. A 5% sulfuric acid solution is circulated in this sampling device by a peristaltic pump. A voltage of 12-14 KV is applied between a thin platinum wire and the wetted wall to induce electrostatic collection. The sampling probe from the sampling nozzle to the WEP was lined with teflon tubing to prevent trace element contamination of the sample. A gas stream is isokinetically drawn from the flue gas stream and through the sampling equipment by a vacuum pump and metered by a dry gas meter. Approximately one hour of sampling was required to obtain sufficient particulate matter for analysis.

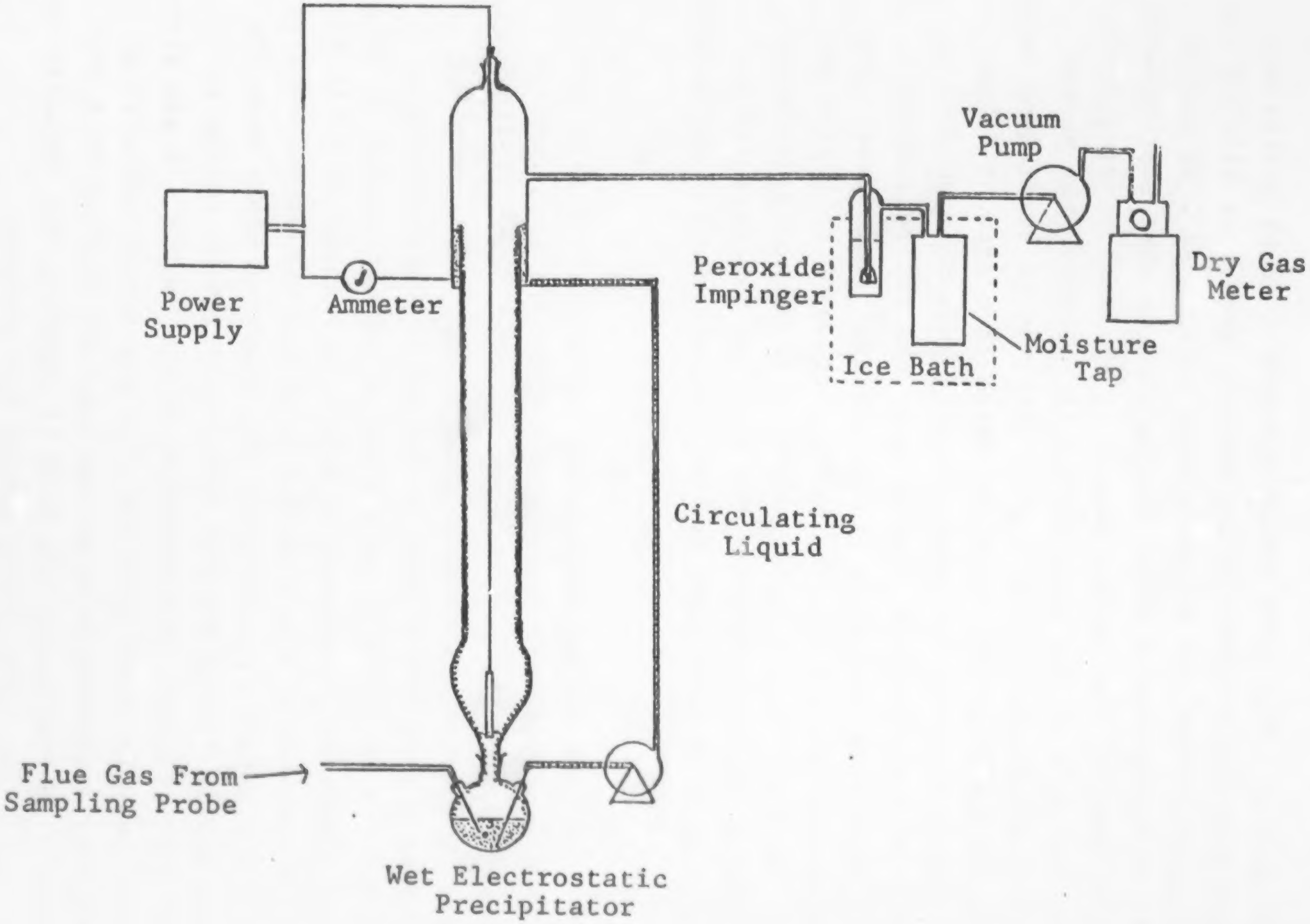

Power Supply
Ammeter
Vacuum Pump
Peroxide Impinger
Ice Bath
Moisture Tap
Dry Gas Meter
Circulating Liquid
Flue Gas From Sampling Probe
Wet Electrostatic Precipitator

FIGURE 3 4

SCHEMATIC OF STATION III
ARRANGEMENG FOR DUCT SAMPLING

In addition to the particulate sampling, a sample for mercury was taken following each WEP sample by diverting the exit gas flow from the WEP through a mesh of gold wire where the mercury is collected by amalgamation with the gold. Samples were also taken during the WEP runs for the determination of the sulfur concentration in the flue gas by bubbling a known volume of gas through a hydrogen peroxide solution according to EPA Method 6. Orsat analysis of the flue gas for oxygen and carbon dioxide was performed to provide gas density information by EPA Method 3.

3.9 Sampling Schedule

The samples and measurements described in the preceding sections were taken during the period August 27, 28, and 29th according to the schedule shown in Figure 3-5. Those samples enclosed in parenthesis are to be analyzed, the rest being retained in reserve.

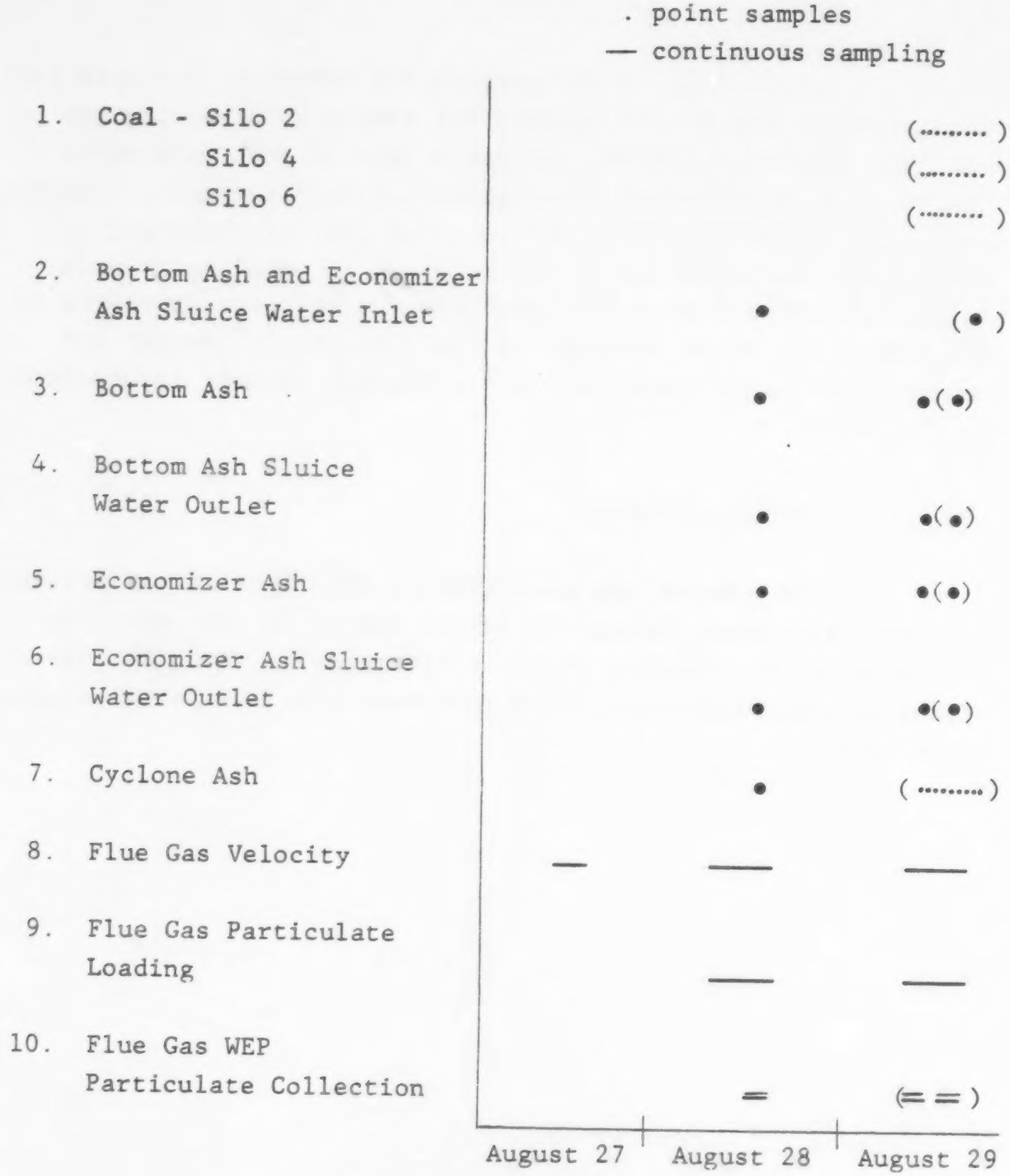


FIGURE 3-5

Sampling Schedule at Station III

4.0 FLOW RATE MEASUREMENTS

The mass flow rate of each of the sampled streams described in Sections 3.0 to 3.8 was determined as described in the following sections.

4.1 Coal

The coal feed was metered by counting the revolutions of the coal feeder which had empirically been determined by plant personnel at a rate of 145 lb. per revolution. The flow rate given by this method must be corrected for the moisture content of the coal to give the rate on a dry weight basis. The rate found from this method roughly checked by comparison with the coal delivery rate to the plant logged from the weighing of the coal trucks. The rate from the coal feeder was found to be 3.71 x 10^5 lb/hr or 2.34 x 10^5 lb/hr on a dry basis after correction for 37% moisture. The coal truck delivery log indicated 4630 tons per day or an average of 3.86 x 10^5 lb/hr delivered to the plant.

4.2 Bottom Ash and Economizer Ash Sluice Water Inlet

The losses in the bottom ash and economizer sluice system were negligible. Therefore, the inlet sluice water flow rate equals the sum of the bottom ash and economizer sluice water outlet rates described in Sections 4.4 and 4.6 The sluice water inlet rate was found to be 2.60 x 10^5 lb/hr.

4.3 Bottom Ash

Determination of the bottom ash production rate directly was impossible because of the difficulty of obtaining a sample of the bottom ash sluice stream which accurately represented the liquid-to-solid ratio in the stream over the entire pumping time. During the periodic pumping time of approximately 30 minutes, the solids content of the sluice stream was high as pumping began and fell off rapidly as the solids in the holding tanks were depleted. The bottom ash production rate was, therefore, determined from the ash content of the coal, the coal feed rate, and the ash accounted for as economizer ash (Section 4.5), cyclone ash (Section 4.7), and fly ash (Section 4.8). From a coal ash content of 11.4% (dry basis), the bottom ash production rate was 1.68×10^4 lb/hr.

4.4 Bottom Ash Sluice Water Outlet

The flow rate of the bottom ash sluice water outlet was determined from the time required to fill a known volume. In this case the known volume was a 12 cubic yard front end loader which was driven into the effluent stream from the sluice pipe so as to catch the entire stream. 30.9 seconds were required to fill the front loader to a level of 178.3 cubic feet giving a flow of 2590 gpm during pumping. If this flow rate is averaged over the four hour pumping cycle, a bottom ash sluice water outlet flow of 1.78×10^5 lb/hr is indicated.

4.5 Economizer Ash

The economizer ash flow rate was determined from the weight percent solids in the economizer ash sluice stream and the volumetric flow rate determined as described for the bottom ash sluice water in Section 4.4. The economizer ash sluice stream required 55.9 seconds to fill the 178.3 cubic foot volume of the front loader to give a flow of 1440 gallons per minute during the pumping time. This flow rate averaged over three four-hour intervals for pumping with an average percent solids in the stream of 0.18% yields an economizer ash production rate in the boiler of 154 lb/hr.

4.6 Economizer Ash Sluice Water Outlet

The flow rate of the economizer ash sluice water outlet stream was determined from the weight percent liquid and the volumetric flow as described in Section 4.5 for the economizer ash flow rate. If the flow rate is averaged over the four hour cycle interval to give an average for the sampling period, we have 8.70×10^4 lb/hr.

4.7 Cyclone Ash

The production rate of cyclone ash in the cyclone dust collector was determined as an average over the 48 hour period from noon on August 27th to noon on August 29th. The level of ash in the cyclone-ash storage silo was measured at the beginning and end of the period. The ash removed from the silo was measured by the record of ash truck weighings over the period. The ash truck weighings were corrected for the water added to the ash to prevent dusting by taking samples from the trucks for moisture content determinations. The difference between the dry ash removed by the ash trucks and the decrease in the quantity of ash remaining in the storage silo is the quantity of ash produced by the cyclones over the 48 hour period.

This total production gives an average production rate of 6.23×10^3 lb/hr.

4.8 Fly Ash and Flue Gas

The flow rate of fly ash from the stack at Station III was determined from the veolocity and particulate loading measurements taken as discussed in Section 3.8. The total amount of flue gas corrected to standard conditions passing through the two ducts is determined from the average gas velocity and the area of the ducts. From the average velocities given in Section 3.8 of 55 fps in the north duct and 67 fps in the south duct, the total flow through both ducts is 6.87×10^5 scfm. The fly ash emissions were then determined from the flow through each duct and an average particulate loading in the north duct of 0.50 gr per scf and in the south duct of 0.65 gr per scf from Section 3.8 to be 3.42×10^3 lb/hr.

4.9 Summary of Flow Rates

The mass flow of each of the sampled streams at Station III is summarized in Table 4-1. The flow rates of all solids are on a dry weight basis.

TABLE 4-1

FLOW RATES FOR STREAMS AROUND STATION III

Stream	Flow Rate
Coal	2.34×10^5 lb/hr.
Bottom Ash and Economizer Ash Sluice Water Inlet	2.65×10^5 lb/hr.
Bottom Ash	1.68×10^4 lb/hr.
Bottom Ash Sluice Water Outlet	1.78×10^5 lb/hr.
Economizer Ash	154 lb/hr.
Economizer Ash Sluice Water Outlet	8.71×10^4 lb/hr.
Cyclone Ash	6.23×10^3 lb/hr.
Flue Gas	4.11×10^7 scfh
Fly Ash	3.42×10^3 lb/hr.

APPENDIX B
ANALYTICAL PROCEDURES

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APPENDIX B

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BIBLIOGRAPHY

Trace element analyses on samples from three power plants were performed using dissolution and analytical techniques adapted specifically for these matrices.

1.0 SAMPLE PREPARATION

Preparation procedures were performed on the following types of samples to provide the primary digestion solution:

Coal
Coal Ash
Sludge
Lime
Wet electrostatic precipitator
Aqueous streams and filtrates

1.1 Coal, Coal Ash, and Sludge Preparation

The dissolution of coal, coal ash, and sludge is achieved by a two-step method. The samples are oxidized at 850-950°C in the presence of air utilizing a quartz pipe reactor. Volatile trace elements are retained via an acetone-dry ice trap at the end of the reactor. Dissolution of the remaining solids is accomplished by treatment with hydrofluoric, nitric, and sulfuric acid. The dissolved solids are then combined with the washings from the cold trap.

1.2 Lime/Limestone Preparation

Lime is dissolved by treatment with 5% hydrochloric acid. Any remaining undissolved material is removed by filtration and treated with hydrofluoric, nitric, and sulfuric acids to achieve dissolution.

1.3 WEP Preparation

An .8μ millipore filter was used to remove particulates from aqueous WEP samples. The particulates were then treated similar to coal (through the quartz pipe reactor acid dissolution steps). The filtrates, dissolved solids, and cold trap washings were quantitatively transferred to a single container to form the primary digestion sample.

1.4 Aqueous Streams and Filtrates Preparation

Nitric acid was added as a preservative to all aqueous samples.

2.0 ANALYTICAL PROCEDURES

The following analytical procedures were utilized for the determination of trace elements in the various samples. Each analytical technique has been screened for accuracy and reliability by standard addition and interference studies.

The complete analytical scheme for the analysis of trace elements in the samples are found in Figures 2-1, 2-2, 2-3, and 2-4. Detection limits for each procedure are summarized in Table 2-1.

2.1 Determination of Fluoride by the Ion-Selective Electrode Technique

The determination of fluoride utilizes a sodium carbonate fusion for solid samples (TH-060) and direct analysis of aqueous samples. The technique of standard addition using a fluoride specific-ion electrode, mentioned by several workers (BA-131, BA-137), is used for measurement of the fluoride ion. A citrate buffer is used to release complexed fluoride ions and to stabilize the pH and ionic strength. Addition of a standard quantity of fluoride is characterized by a change in the potential of the solution. The specific ion electrode senses this change in potential which is related to the initial fluoride concentration. The relationship between potential and fluoride concentration follows the Nernst equation:

$$\Delta E = A \log (C_T + X_i)/C_T$$

where,

ΔE is the change in potential

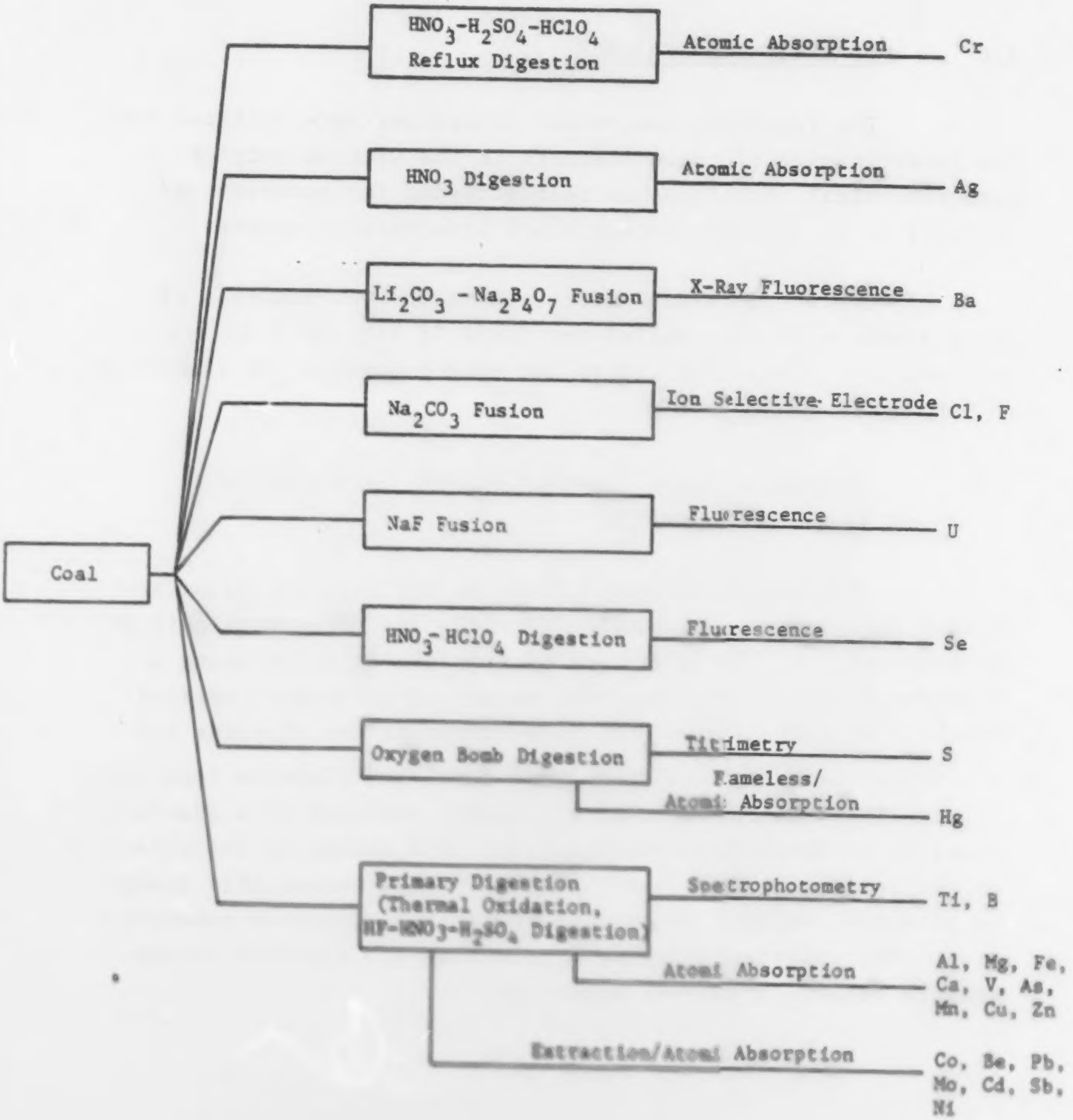
Coal
HNO3-H2SO4-HClO4 Reflux Digestion
Atomic Absorption
Cr
HNO3 Digestion
Atomic Absorption
Ag
Li2CO3 - Na2B4O7 Fusion
X-Ray Fluorescence
Ba
Na2CO3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO3- HClO4 Digestion
Fluorescence
Se
Oxygen Bomb Digestion
Titrimetry
S
Flameless/ Atomic Absorption
Hg
Primary Digestion (Thermal Oxidation, HF-HNO3-H2SO4 Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni

FIGURE 2-1

ANALYSIS PROCEDURE FOR TRACE ELEMENT ALYSIS

OF COAL

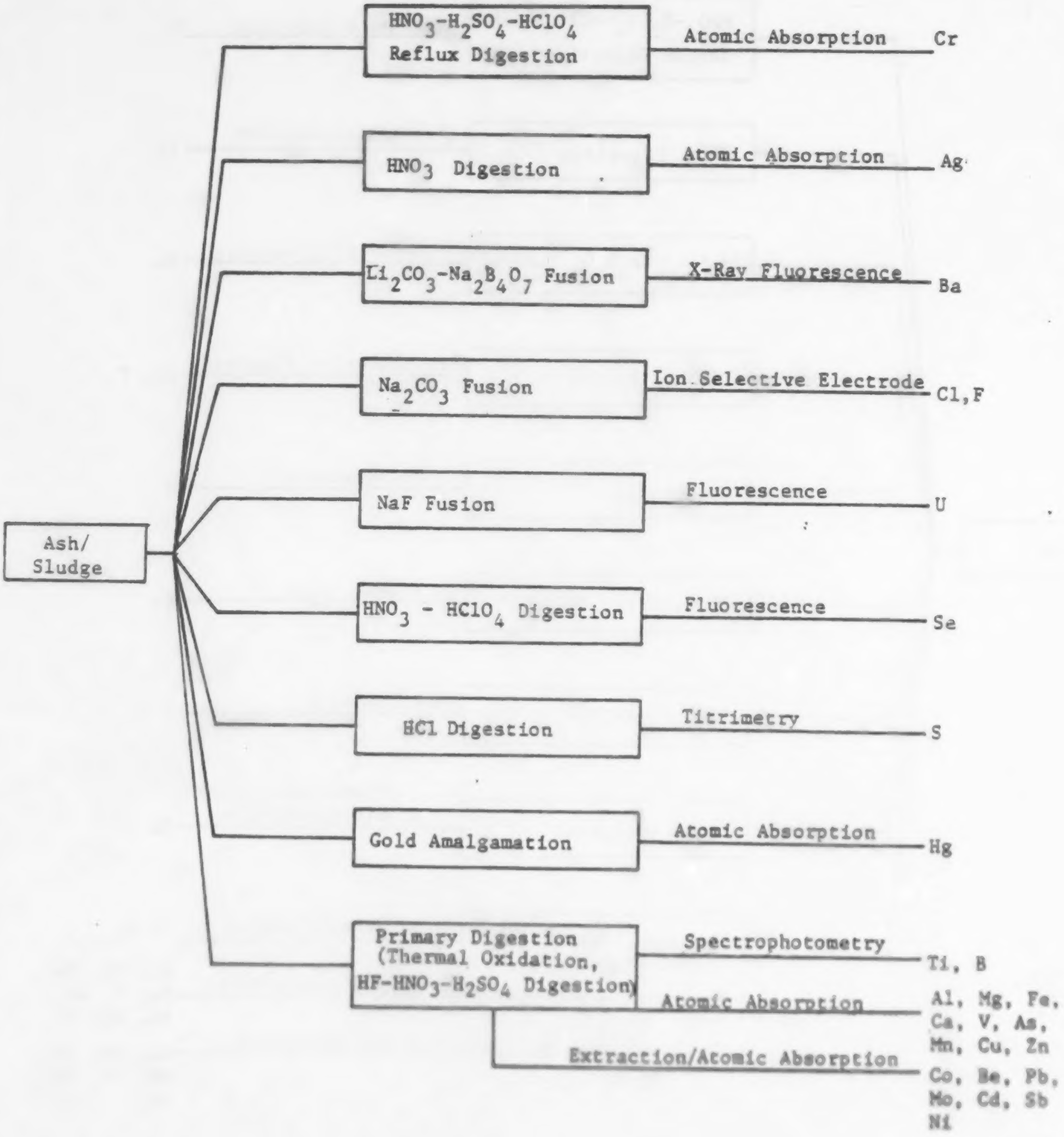
Ash/ Sludge
HNO_3-H_2SO_4-$HClO_4$ Reflux Digestion
Atomic Absorption
Cr
HNO_3 Digestion
Atomic Absorption
Ag
Li_2CO_3-$Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
Na_2CO_3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO_3 - $HClO_4$ Digestion
Fluorescence
Se
HCl Digestion
Titrimetry
S
Gold Amalgamation
Atomic Absorption
Hg
Primary Digestion (Thermal Oxidation, HF-HNO_3-H_2SO_4 Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb Ni

FIGURE 2-2

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS
OF COAL ASH AND SLUDGE

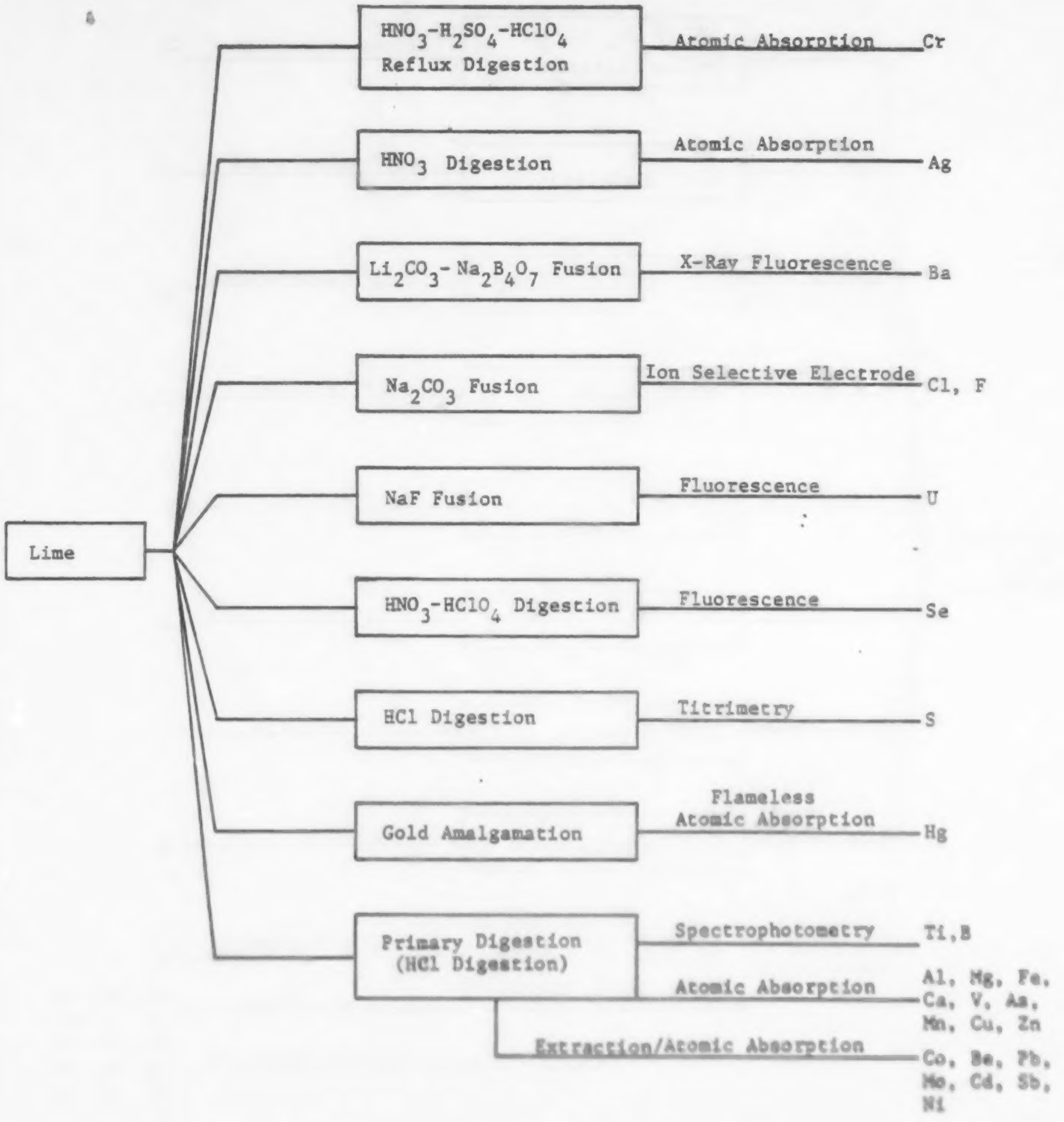
Lime
HNO_3-H_2SO_4-$HClO_4$ Reflux Digestion
Atomic Absorption
Cr
HNO_3 Digestion
Atomic Absorption
Ag
Li_2CO_3- $Na_2B_4O_7$ Fusion
X-Ray Fluorescence
Ba
Na_2CO_3 Fusion
Ion Selective Electrode
Cl, F
NaF Fusion
Fluorescence
U
HNO_3-$HClO_4$ Digestion
Fluorescence
Se
HCl Digestion
Titrimetry
S
Gold Amalgamation
Flameless Atomic Absorption
Hg
Primary Digestion (HCl Digestion)
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn
Extraction/Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni

FIGURE 2-3

ANALYTICAL PROCEDURE FOR TRACE ELEMENT ANALYSIS OF LIME

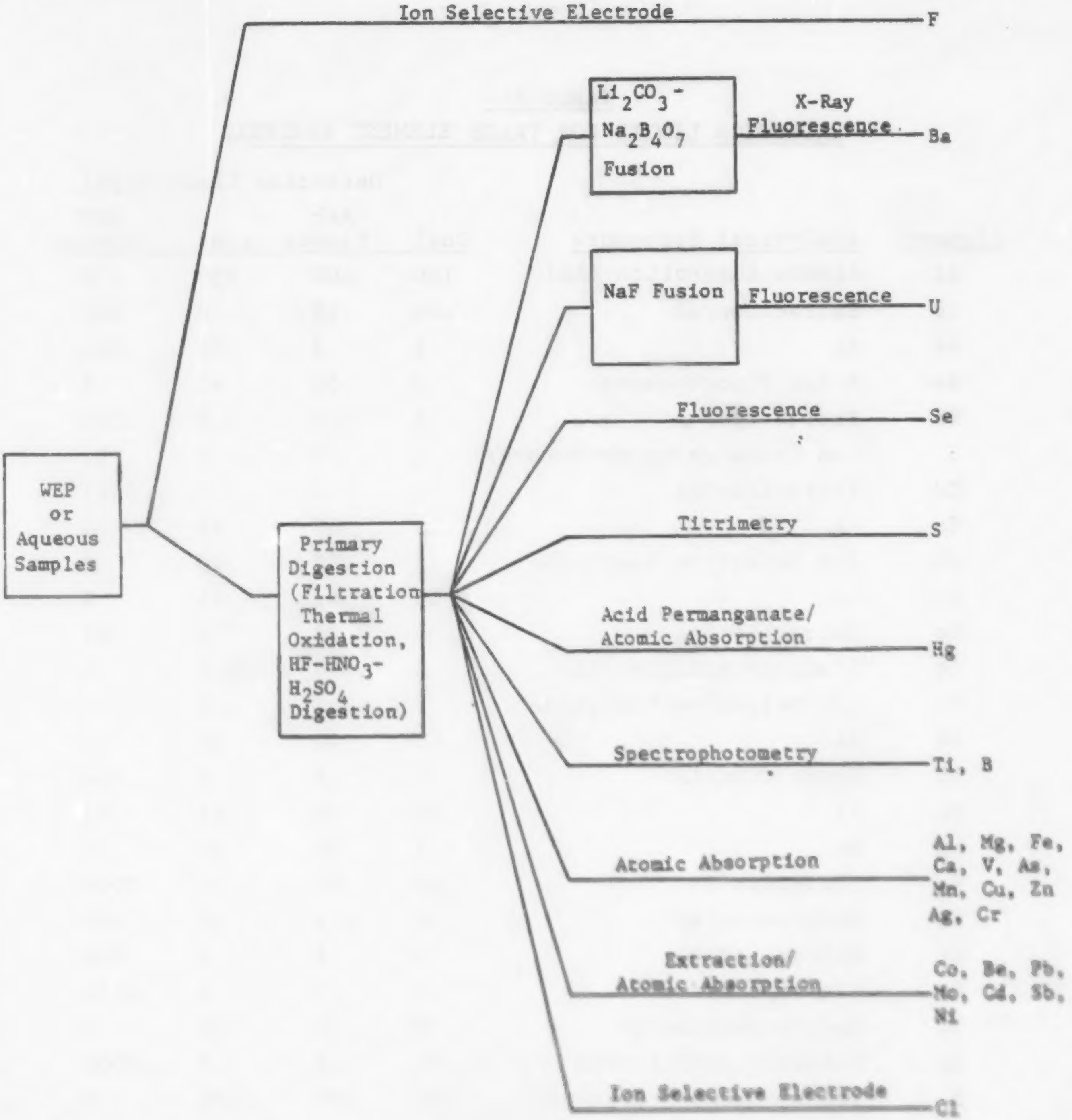
Ion Selective Electrode
F
Li2CO3-Na2B4O7 Fusion
X-Ray Fluorescence
Ba
NaF Fusion
Fluorescence
U
Fluorescence
Se
WEP or Aqueous Samples
Titrimetry
S
Primary Digestion (Filtration Thermal Oxidation, HF-HNO3-H2SO4 Digestion)
Acid Permanganate/ Atomic Absorption
Hg
Spectrophotometry
Ti, B
Atomic Absorption
Al, Mg, Fe, Ca, V, As, Mn, Cu, Zn Ag, Cr
Extraction/ Atomic Absorption
Co, Be, Pb, Mo, Cd, Sb, Ni
Ion Selective Electrode
Cl

FIGURE 3-4

ANALYTICAL PROCEDURES FOR TRACE ELEMENT ANALYSIS OF WET ELECTROSTATIC PRECIPITATOR LIQUORS AND AQUEOUS SAMPLES

TABLE 2-1

DETECTION LIMITS FOR TRACE ELEMENT ANALYSIS

Element	Analytical Procedure	Detection Limit (ppm) Coal	Ash Sludge	Lime	WEP Aqueous
Al	Atomic Adsorption (AA)	100	400	650	1.0
Sb	Extraction/AA	.04	.16	.6	.002
As	AA	.1	.5	.06	.001
Ba	X-Ray Fluorescence	5	50	40	.5
Be	Extraction/AA	.2	1.6	1.0	.001
B	Ion Exchange/Spectrophotometry	1	3	3	.05
Cd	Extraction/AA	.1	.2	.2	.0002
Ca	AA	10	40	65	.1
Cl	Ion Selective Electrode	5	10	10	.5
Cr	AA	10	40	65	.1
Co	Extraction/AA	.2	.8	1	.003
Cu	Standard Addition/AA	1	4	6.5	.1
F	Ion Selective Electrode	.5	1.2	1.2	.1
Fe	AA	10	40	65	.1
Pb	Extraction/AA	.4	.8	5	.004
Mn	AA	10	40	65	.01
Mg	AA	5	20	30	.5
Hg	Flameless AA	.01	.01	.01	.0005
Mo	Extraction/AA	.4	1.6	16	.004
Ni	Extraction/AA	2	8	2	.006
Se	Fluorometry	.1	.1	.1	.0005
Ti	Spectrophotometry	5	20	20	.1
Ag	Standard Addition/AA	.05	.2	.3	.0005
S	Ion Exchange/Titrimetry	100	100	200	5
U	Fluorometry	.0001	.0001	.0001	.0001
V	Standard Addition/AA	1	4	6.5	.005
Zu	Standard Addition/AA	1	4	6.5	.01

A is the constant = 59 mV at 25°C

C_F is concentration of free fluoride in solution

X_i is additional fluoride concentration added.

2.2 Determination of Chloride by Ion-Selective Electrode

Chloride is determined by a known standard addition method (OR-016). Sample preparation is the same as fluoride with a sodium carbonate fusion for all solid samples and direct analysis of aqueous solutions. A known amount of the species being measured is added to a known volume of sample and the resulting change in potential is observed. The original sample concentration is computed using a known addition table. The method allows samples to be analyzed which have variable ionic strength.

2.3 Spectrophotometric Determination of Titanium

Titanium is determined in the primary digestion solution as a yellow complex formed with tiron (disodium -1, 2- dihydroxybenzene -3, 5- disulfonate). This method is based on the procedure of Yoe and Armstrong, and is further extended to include shales by Rader (RA-125). An acetate buffer is used to regulate the pH. The only major interference is the complex tiron forms with Fe. This interference is eliminated by addition of sodium dithionite, reducing ferric to ferrous ion. The absorbance of the complex is read on a double beam spectrophotometer and samples compared with a standard calibration curve.

2.4 Determination of Copper and Zinc by Atomic Absorption

Copper and zinc are determined by direct aspiration of the primary digestion into the flame of the atomic absorption spectrophotometer (PE-115). Quantitative determinations are achieved by comparing the samples to their respective standards and by the use of standard additions to the primary digestions.

2.5 Determination of Molybdenum by Atomic Absorption

Molybdenum analysis is based on organic extraction atomic absorption technique and method of Joyner (JO-012) which has been modified by Kinrade and Van Loon (KI-085). Molybdenum in the primary digestion readily forms a complex with ammonium pyrrolidinedithiocarbamate at an acidic pH. Extraction of this complex with methyl isobutyl ketone offers a convenient method of concentration of the element. The signal is further enhanced by use of a nitrous oxide-acetylene flame. Concentration was determined by use of a standard calibration curve.

2.6 Determination of Nickel and Cobalt

Nickel and cobalt analyses are based on the organic extraction atomic absorption technique and method of Joyner (JO-012). An ammonium tartrate buffer is used to stabilize the primary digestions. Nickel and cobalt are complexed with the chelating agent sodium diethyldithiocarbamate and extracted with methyl isobutyl ketone.

Once the metal complex has been separated and concentrated in the organic phase, the solution can be directly aspirated into atomic absorption spectrophotometer for measurement of the metal concentration.

2.7 Determination of Arsenic by Flameless Atomic Absorption

Arsenic is determined by a Radian modified flameless atomic absorption procedure based on the method of Ramakrishna, Robinson and West (RA-147) incorporation the techniques of Ediger (ED-027). The usually volatile arsenic present in the primary digestion is complexed as the molybdenum heteropoly acid with ammonium molybdate in a nitric acid medium. The complex formation enables the complex to be analyzed on the graphite furnace by reducing the volatility of the arsenic so that high temperature charring can be used to rid the sample of matrix interferences.

2.8 Determination of Antimony by Flameless Atomic Absorption

Antimony determination is based on a Radian flameless atomic absorption method modifying the extraction procedure of Burke (BU-136) and Headridge and Smith (HE-094) while utilizing the techniques of Ediger (ED-027) to reduce the volatility of antimony. After complexation with iodide, antimony is extracted from the primary digestion into a methyl isobutyl ketone and tributyl phosphate mixture (MIBK-TBP). TBP increases the extraction efficiency. As with arsenic, ammonium molybdate is used to increase the thermal stability of the complex during the charring cycle in the graphite furnace.

2.9 Determination of Beryllium by Atomic Absorption

The method of Bokowski (BO-027) is used for the determination of beryllium by atomic absorption. After addition of EDTA to the primary digestion to mask interferences, the beryllium present in the aqueous sample is chelated with acetylacetone. The complex is then extracted with methyl isobutyl ketone and the organic phase directly aspirated into the atomic

absorption spectrophotometer for the determination of beryllium. The solvent extraction procedure allows one to conveniently separate and concentrate the beryllium present.

2.10 Fluorometric Determination of Uranium

Radian's uranium procedure is a modification of the fluorometric determination of Thatcher (TH-049) updated by Turner (TU-025). Hexavalent uranium ions have a native fluorescence that may be used for analysis in relatively high concentrations. However, when fused with fluoride salts, uranyl ions produce an intense specific fluorescence detectable at levels of 10^{-10} grams of uranium. In general, the solid sample is mixed with a sodium fluoride flux and fused to a translucent disc in a platinum crucible. Aqueous primary digestions are evaporated in platinum crucibles and the residue fused with the flux. Once cooled, its fluorescence is measured with a Turner filter fluorometer. The method of standard additions is used to compensate for quenching.

2.11 Determination of Lead and Cadmium by Atomic Absorption

The procedure for analysis of lead and cadmium is similar to that for copper and zinc found in Section 2.4. Trace elements present in the primary digestion are separated and concentrated by chelation and extraction. Kinrade and Van Loon's method (KI-085) utilizing two chelating agents, ammonium pyrrolidinedithiocarbamate (APDC) and diethyl ammonium diethyldithiocarbamate (DDDC) to complex lead and cadmium has been highly successful. A citrate buffer was used due to its stability, strong buffering capacity, and nonparticipation in any reaction. The sample solution was extracted into methyl isobutyl ketone

and the organic solution injected into the graphite furnace on the atomic absorption spectrophotometer. Concentration was determined by use of a standard calibration curve.

2.12 Fluorometric Determination of Selenium

Selenium in the form of selinite reacts with aromatic orthodiamines to form piazselenols which fluoresce in various organic solvents. This method of determination of selenium is a Radian modification of a procedure published by Levesque and Vendette (LE-068). The solid sample is digested with nitric and perchloric acids in the Parr acid digestion bomb (HA-258). Aqueous samples are heated with nitric and perchloric acids. In both cases this oxidizes selenium to selenate and is followed by hydrochloric acid reduction to selinite. Isolation of selenite from interferring substances is accomplished by adding hydroxylamine, EDTA, and formic acid. The selenite is then reacted with 2, 3-diaminonaphthalene to form the organic extractable piazselenol, naphtho-(2, 3-d)-2 selena-1, 3-diazole, which is determined fluorometrically. This method is free of any interferences and is capable of detecting nanograms of selenium by use of a calibration curve.

2.13 Determination of Vanadium and Silver by Flameless Atomic Absorption

Vanadium is determined by flameless atomic absorption using the heated graphite atomizer. The method is a Radian adaptation of the work of Cioni, Innocente and Mazzioli (CI-002). Standard additions are performed on the primary digestion solution. Experimentation conducted on National Bureau of Standards samples of coal and coal ash yield results within 10% of the certified values.

Huffman (HU-095) recommends the same procedure for silver. Solid samples are dissolved in concentrated nitric acid and the method of standard additions is utilized.

2.14 Determination of Barium by X-ray Fluorescence

Barium is determined by a Radian method utilizing X-ray fluorescence. Samples are pelletized in a solid flux of lithium carbonate-sodium borate which are then introduced directly into the X-ray unit. Quantitative determinations are achieved by comparing the samples to a barium standard calibration curve prepared in the same manner and by the use of the method of standard additions to correct for matrix interferences, if any are present.

2.15 Determination of Chromium, Calcium, Iron, Magnesium, Manganese and Aluminum by Atomic Absorption

Chromium, calcium, iron, magnesium, manganese and aluminum (PE-115) are determined by direct aspiration into the flame of the atomic absorption spectrophotometer. Calcium and magnesium are diluted with lanthanum chloride to ease interferences. All elements are compared with standard calibration curves. All analyses are performed on the primary digestion solutions except chromium.

Chromium requires a special preparation for solid samples. Digestion of coal, ash, limestone, and sludge is accomplished with nitric, sulfuric, and perchloric acids in a reaction flash. A packed reflux column is attached to prevent any loss of chromium. Perchloric acid oxidizes all the chromium to Cr^{+6}. This method was developed by Raine and Menis (RA-133) as a mercury determination procedure. Radian has applied the method to the determination of chromium in NBS standard reference

materials of coal and coal ash and the results were comparable to the reported values.

2.16 Determination of Mercury by Flameless Atomic Absorption

Two methods were used for mercury analysis:

(1) acid permanganate

(2) gold amalgamation

Mercury is determined by a flameless atomic absorption technique. Liquid samples are treated with acid potassium permanganate to oxidize all of the mercury present to the +2 oxidation state. The excess $KMnO_4$ is removed with the addition of hydroxylamine hydrochloride, and the Hg^{+2} is reduced to elemental mercury by the addition of stannous chloride, which is swept through the absorption cell of the atomic absorption unit for determination.

Gold amalgamation collection of mercury has been reported by several workers (KA-086, DI-043). Radian utilizes a double amalgamation technique in which mercury is collected on a gold wire plug in a quartz tube either from flue gas passed through the tube or from thermal desorption into a stream of argon from solid samples. The mercury thus collected is desorbed by heating and amalgamated on a second tube to minimize interferences. Upon desorption from the second tube, the mercury is passed into an absorption cell positioned in the atomic absorption spectrophotometer.

2.17 Sulfur Determination by Titrimetry

The method of sulfur analysis consists of determining the total sulfur as sulfate by titrimetry. Initial sample preparation for coal is performed by ignition in a Parr Ignition Bomb and sorption of the evolved SO_2 in a sodium carbonate solution. Sludge and ash samples are mixed with hydrochloric acid and the solids filtered. In both cases, hydrogen peroxide is added to oxidize sulfite to sulfate. The sample is passed through a cation exchange column to form sulfuric acid. The acid is titrated with standard sodium hydroxide and the sulfur concentration determined.

Nitrate and phosphate ions interfere. Heat applied with hydrochloric acid at pH 2-4 avoids nitrite interference in the column. If the sample is heated at 275°C for 30 minutes to drive off sulfuric acid, phosphate can be determined and the value subtracted from the total to give sulfate ions.

2.18 Spectrophotometric Determination of Boron

Radian's boron procedure combines the separation method of Carlson (CA-084) and the spectrophotometric determination of Mair and Day (MA-190). An ion-exchange column is prepared using a boron specific resin, Amberlite XE-243, to separate boron in the primary digestion from interfering ions and allow complete boron recovery. It is then extracted into chloroform with 2-ethyl-1, 3-hexanediol. Boron in the organic phase is converted to the highly absorbing rosocyanin complex using glacial acetic acid followed by sulfuric acid. The absorbance of the complex is read on a double-beam spectrophotometer and samples compared with a standard calibration curve.

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